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INSTABILITY OF SOLUTIONS OF HIGH POLYMERS[1]

BY J. A. MORRISON[2], J. M. HOLMES[3], AND R. MCINTOSH[4]

Abstract

The change in the viscosity property of solutions of high polymers on ageing has been investigated. It has been found that the variations in viscosity are due to changes in the molecular weight of the dissolved polymer, caused by the presence of small amounts of impurities. In particular, oxygen appears to give rise to degradation reactions, while iron salts cause the formation of gel structures. Solutions of the dry polymers in pure solvents, when aged in the absence of air, show only very small variations in viscosity. The investigation has been conducted with three polymers, polyvinyl acetate, polystyrene, and polymethyl methacrylate in solution in three solvents, bis(2-chloroethyl) ether, nitrobenzene, and bis(2-chloroethyl) sulphide.

The principal reaction seems to occur between the impurity and the polymer, with the solvent acting as an inert medium. However, it appears that in the case of bis(2-chloroethyl) sulphide, reaction of iron salts with the solvent is possible.

The intrinsic viscosity of polyvinyl acetate recovered from the aged solutions has been determined. The k' factor of Huggins has been evaluated from these measurements, and appears to change during some of the ageing processes.

Introduction

Several instances of instability in solutions of high polymers are recorded in the literature, and have been observed generally as changes in the viscosity property. Mead and Fuoss (4) report viscosity instability for solutions of polyvinyl chloride in methyl amyl ketone and cyclohexanone, and attribute the changes in viscosity to the untangling and elongating of the polymer chains. Wehr (9) states that the stability of solutions of polyvinyl chloride in several solvents depends upon the degree of saturation of the polymer, the light intensity, and the presence of acids, bases, and catalysts. Blaikie and Crozier (2) aged solutions of polyvinyl acetate in glacial acetic acid in glass bombs at 160° C., and observed an initial decrease in the viscosity, followed by an increase at the end of four weeks, the changes being smaller when air was excluded.

Bartell and Cowling (1) found that the introduction of various metals as salts into alkali cellulose altered the rate of lowering of viscose viscosity with length of time of ageing the alkali cellulose. Manganese (and iron to a lesser extent) increased the rate of change of viscosity by increasing the rate of

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Contribution from the Department of Chemistry, McGill University, Montreal, Que.
[2] *At the time, holder of a Fellowship under the National Research Council of Canada.*
[3] *At the time, holder of a Studentship under the National Research Council of Canada.*
[4] *Honorary Sessional Lecturer.*

depolymerization of the cellulose by oxygen. Further evidence of the effect of oxygen comes from the work of Naunton (6) on rubber photogels. When solutions containing rubber were exposed to light in the presence of an excess of oxygen, the oxygen was absorbed slowly and the viscosity of the solutions decreased to a limiting value. While the type of degradation was similar in all solutions, the extent of the change was dependent partly upon the solvent.

The present investigation arose through the necessity of storing solutions of high polymers in technical solvents for long periods in iron containers. For this reason, the effects of iron salts and of air were studied extensively. An ageing temperature of 60° C., which was thought to be the highest encountered in normal storage, was used throughout. The greater portion of the results was derived from systems containing polyvinyl acetate, which was of more practical interest to the investigation. The change in the viscosity property of the solutions was used as a measure of stability, which limits the expression of the results in a quantitative manner.

Experimental

Viscosity Measurements

Measurements were made with three types of viscometers. To measure the viscosity of the aged solutions, a U-tube capillary viscometer, developed at Porton, England, was used. Results could be reproduced to better than 1% with this instrument, which had the advantage that only a very small sample (about 0.5 cc.) was required. To detect the presence of gel structure, and to measure deviations from Newtonian flow properties in the polymer solutions, a modified Ubbelohde (8) suspended level viscometer was employed. From the dimensions of the instrument and from the Hagen–Poiseuille formula it was possible to derive values for the rate of shear and the shear stress to which the liquids were subjected. The presence of structure was indicated when a plot of the shear stress against the rate of shear showed an intercept on the shear stress axis. The intrinsic viscosity of polyvinyl acetate was derived from measurements in dilute solution in acetone, using the conventional Ostwald viscometer. The data were plotted in the form $\frac{\ln \eta_r}{c}$ versus c, where η_r = relative viscosity and c = concentration in grams per 100 cc. of solution. Extrapolation to zero concentration gave the intrinsic viscosity. The k' factor was derived from the relation of Huggins (3) $k' = \frac{1}{2} - \frac{\text{slope}}{[\eta]^2}$.

All viscosity measurements were made at 20° C.

Materials

Three types of polymers were studied:

Polyvinyl acetate (Gelva V-45, Shawinigan Chemicals Ltd.).

Polymethyl methacrylate (NDR-359, E. I. duPont de Nemours).

Polystyrene (Styron A-200, Dow Chemical Co.).

The polymers were dried for 48 hr. *in vacuo* before being dispersed in the solvents. Insoluble material was removed by filtering the viscous solutions

rapidly through a mat of glass wool. The saponification values of samples of polyvinyl acetate were determined by the method of Minsk *et al.* (5).

The solvents, with the exception of bis(2-chloroethyl) sulphide, were obtained by distilling the technical materials *in vacuo*. Bis(2-chloroethyl) sulphide was prepared by the reaction of concentrated hydrochloric acid with thiodiglycol, with subsequent distillation *in vacuo*. The purified solvents were stored over "Drierite."

Anhydrous ferric chloride was prepared by passing a stream of dry chlorine diluted with nitrogen over iron powder heated to a dull red in a Pyrex tube. The shiny black crystals of ferric chloride were collected from the cool part of the tube, and were stored in a vacuum desiccator. Analysis showed the material to be 99% pure. Anhydrous ferrous chloride was prepared in a similar manner by using dry hydrochloric acid gas, and by analysis was 98% pure.

Ageing Procedure

Throughout the investigation an effort was made to keep the systems free from moisture. The viscous solutions were prepared in closed vessels equipped with mercury seal stirrers. In preparing the solutions containing varying concentrations of iron, the salt was added quickly to a weighed portion of the solvent. This solution was diluted with a measured quantity of polymer solution to give a desired concentration of iron salt.

For the most part, the viscous solutions were aged in sealed glass bombs. A few comparative experiments were performed using glass stoppered bottles as containers. The bombs were equipped with two side-arms and a stirrer consisting of a nail sealed within a piece of glass tubing. Each bomb was filled with approximately 100 cc. of viscous solution through one of the side-arms. This arm was sealed off, and the other was connected through a ground glass joint to a vacuum line operating at a pressure of 0.005 mm. of mercury. The solution was degassed with stirring until the pressure was equal to the vapour pressure of the solvent. In any one series of experiments, the time of evacuation for each bomb was kept constant, so that solvent losses were the same in each case. The bombs were sealed off under vacuum, and set to age in a large air-bath controlled to $60 \pm 0.1°$ C. At appropriate intervals bombs were removed from the bath, and cut open, after which the viscosity of each solution was measured. In the case of the polyvinyl acetate series the polymer was recovered and compared with the original material on the basis of intrinsic viscosity and in some cases on the basis of saponification value.

Two methods of recovering the polyvinyl acetate were tried. The first of these consisted of steam distilling the solutions of polyvinyl acetate in bis(2-chloroethyl ether), but it was found that the process hydrolysed part of the polymer, as shown by low and irregular saponification values and yields. This may have been caused by hydrochloric acid from hydrolysis of the solvent. A second method, using organic precipitants, proved to be quite

satisfactory. The viscous solution was poured slowly into an excess (6 : 1 by volume) of petroleum ether (30° to 60° C. fraction) which was stirred violently. The precipitated polymer was dissolved in benzene (100 cc. per 8 gm. of polymer) and again brought down in petroleum ether under similar conditions. Excess solvent was drawn off under vacuum, after which the polymer was dissolved in acetone (100 cc. per 8 gm. of polymer), and precipitated in a large excess of water. The porous mass was dried to constant weight *in vacuo*, and cut into small pieces. The yield was generally within 2% of the theoretical, and the saponification value was unchanged by the process.

Results

The experimental data may be divided into two sections. The first deals with the system polyvinyl acetate–bis(2-chloroethyl) ether, while the second is concerned with the extension of the investigation to the other polymer–solvent systems.

A. Initially, solutions of Gelva V-45 in pure bis(2-chloroethyl) ether were aged at 60° C. in sealed bombs in the absence of air. The data for two such series are given in Tables I and II. In Table II, the polymer viscosity denotes the viscosity of a standard solution of the polymer in benzene (86 gm. per litre of solution).

In both series (Tables I and II) the changes in viscosity are small. In Table I the upward trend in viscosity is followed by a similar trend in the

TABLE I

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	% Recovery of polymer	Intrinsic viscosity	k'
0	5.55	99.5	1.05	0.37
14	5.70	99.0	1.12	0.33
28	5.70	98.0	1.11	0.33
60	5.75	100.0	1.09	0.35
104	5.85	98.5	1.13	0.35
188	5.90	—	1.12	0.35

TABLE II

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	% Recovery of polymer	Polymer viscosity, centipoises	Saponification value, %
0	4.90	99.5	52.9	98.5
8	4.55	100.0	48.2	99.5
19	4.65	98.5	51.2	96.5
54	4.75	97.0	54.5	97.0

intrinsic viscosity of the recovered polymer within experimental error. The k' value also changes during the ageing process, but the variation is hardly consistent enough to be significant. In Table II the change in viscosity of the thickened solutions is followed by a similar change in the polymer viscosity. At the same time the saponification values vary, but in an irregular manner. This can probably be attributed to the method of determination.

For comparison, in Table III are shown data for similar solutions aged in bombs of which only the headspaces were evacuated, and in glass stoppered bottles.

TABLE III

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	
	Bombs	Glass bottles
0	3.70	3.80
11	3.05	2.20
25	3.00	1.40
30	2.95	—
74	—	0.30

A decrease in viscosity is observed for both types of storage, the change being greater in the glass bottles. In conjunction with the data in Tables I and II, three ageing conditions are represented; absence of air, limited amount of air, and unlimited amount of air. The results indicate then that the polymer solutions are degraded only when air is present. The materials were dried before the preparation of the thickened solutions; this seems to eliminate the possibility that the effect is caused by water vapour. Oxygen appears then to be the degrading agent, in agreement with the findings of other workers (1, 2). Preliminary experiments on the ageing of solid polyvinyl acetate in an atmosphere of oxygen indicate that the polymer is degraded (10).

A large sample of a solution of Gelva V-45 in bis(2-chloroethyl) ether was aged in a stoppered flask at 60° C. At intervals the polymer was separated from small portions of the solution, after which the intrinsic viscosity of the polymer was measured. The data are shown in Table IV.

TABLE IV

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	Intrinsic viscosity	k'
0	3.70	1.07	0.34
8	3.50	1.03	0.34
87	3.25	0.98	0.36
154	3.15	0.95	0.33

The change in viscosity is not as large as that shown in the second column of Table III. This is probably due to the fact that the flask was nearly filled with liquid, and as a result the ratio of the volume of air to the volume of liquid was small compared with that existing in glass stoppered bottles. The important point is that the change in viscosity is paralleled by a similar change

TABLE V

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER PLUS 0.003% FERRIC CHLORIDE

Ageing time, days	Viscosity, poises	Intrinsic viscosity	k'
0	3.55	1.01	0.34
1	5.45	1.24	0.37
$2\frac{1}{2}$	8.70	1.59	0.38
3	12.0	1.66	0.39
5	13.3	1.72	0.39

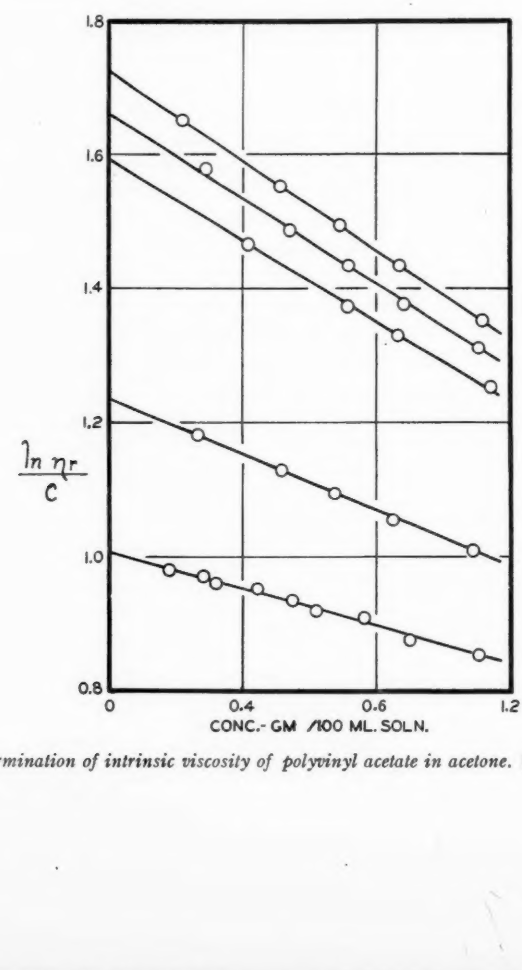

FIG. 1. *Determination of intrinsic viscosity of polyvinyl acetate in acetone.* $[\eta] = \lim_{c \to 0} \frac{\ln \eta_r}{c}$

in the intrinsic viscosity of the recovered polymer. This suggests that the molecular weight of the polymer is lowered in the ageing process. The k' value has changed during ageing but again the change is irregular and may not be significant.

The effect of iron salts was noted first when approximately 0.25% of ferric chloride was added to a solution of Gelva V-45 in bis(2-chloroethyl) ether and caused the formation of a gel. Many such experiments were performed but it will suffice to set down typical results. In Table V data are recorded for a series of solutions containing 0.003% of anhydrous ferric chloride, which were sealed in bombs at a pressure of 0.1 mm. of mercury.

A threefold increase in viscosity is paralleled by a large increase in the intrinsic viscosity of the recovered polymer. This again suggests that the change in the original solution on ageing is due to a change in the molecular weight of the dissolved polymer. These data are plotted in Figs. 1 and 2.

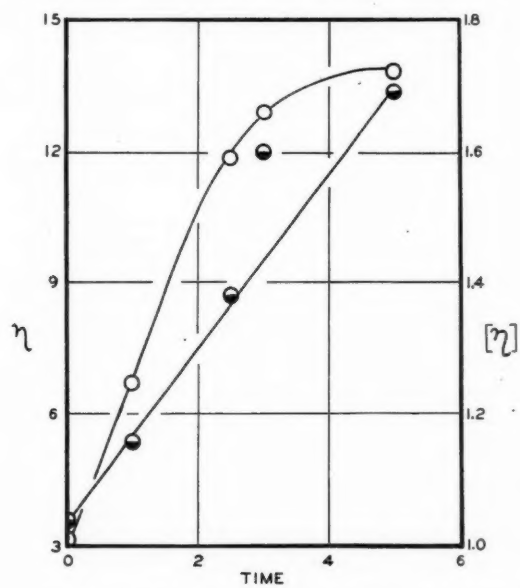

FIG. 2. ◒——◒ *change of viscosity of solutions of Gelva V-45 in bis(2-chloroethyl) ether plus 0.003% ferric chloride on ageing.*
○——○ *change of intrinsic viscosity of the recovered polyvinyl acetate.*

The k' value shows an upward trend which may be construed as a change in the average shape or configuration of the polymer. It is of interest to compare the intrinsic viscosity and k' of a higher molecular weight polyvinyl acetate, Gelva V-150, with those in Table V. The $[\eta]$ and k' of Gelva V-150 are 1.82 and 0.37 respectively, which are not very different from the values for the last

sample in Table V. This supports the view that the change in intrinsic viscosity represents a change in molecular weight.

When solutions of Gelva V-45 in bis(2-chloroethyl) ether containing more than 0.005% of ferric chloride were sealed in evacuated glass bombs, only a viscosity increase was observed, while in glass bottles a decrease in viscosity was observed first. In either case, the end result was a firm gel. This is illustrated by the data in Table VI.

TABLE VI

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises		
	Plus 0.1% $FeCl_3$ in bombs	Plus 0.01% $FeCl_3$ in bottles	Plus 0.1% $FeCl_2$ in bottles
0	7.3	4.1	5.0
½	10.3	—	—
1	Gel	—	—
4	—	—	4.5
12	—	2.3	1.9
23	—	2.6	2.7
28	—	—	Gel
31	—	4.5	—
36	—	4.6	—
38	—	Gel	—

The viscosities of these solutions were measured in the Ubbelohde viscometer, and it was observed that deviations from Newtonian flow were obtained only when the viscosity was increasing. This is shown in Fig. 3, where the data from the third column of Table VI are plotted. An intercept on the shear stress axis first appears with the third sample. Within the limit that this method can detect structure, it appears that the degradation and the gel forming reactions are independent of each other.

In the presence of air, ferrous chloride caused effects similar to those of ferric chloride (Column 4, Table VI). This is undoubtedly due to the oxidation of the ferrous salt to the ferric form by air. In evacuated bombs, ferrous chloride caused a gradual increase in viscosity, as is shown in Table VII. Many similar solutions aged in evacuated bombs were aged for periods up to six months without appearance of gel structures, in clear contrast to the behaviour with ferric chloride.

The polymer viscosity increases in keeping with the increase in the viscosity of the original solution. This is a behaviour similar to the change in intrinsic viscosity shown in Table V. At the same time, the change in saponification value is small and irregular. What change does occur is probably within the limit of accuracy of the saponification method. The change in viscosity cannot then be due to a hydrolytic reaction.

TABLE VII

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER PLUS 0.1% FERROUS CHLORIDE

Ageing time, days	Viscosity, poises	% Recovery of polymer	Polymer viscosity, centipoises	Saponification value, %
0	5.20	100.0	51.0	98.5
7	6.05	98.5	62.5	98.0
20	6.60	96.5	67.1	98.0
32	6.95	98.0	69.7	97.0

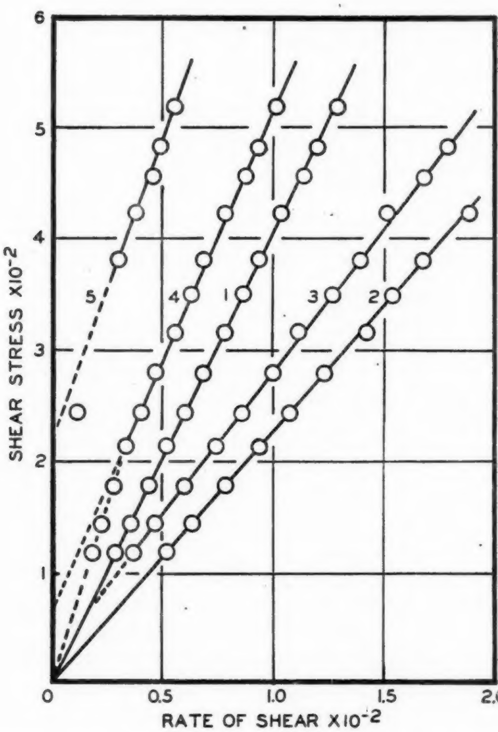

FIG. 3. *Typical plot of shear stress against rate of shear derived from viscosity measurement with the Ubbelohde viscometer.*

B. To test the generality of viscosity instability, solutions of the three polymers in three solvents were prepared. To these solutions were added various concentrations of ferric or ferrous chloride, and samples of each solution were aged both in evacuated bombs and in glass stoppered bottles. The viscosity of the solutions in the bottles was measured at intervals, while

for the bombs, only the time of gel formation was recorded. The data are summarized in Table VIII.

TABLE VIII

THE AGEING OF SOLUTIONS OF GELVA V-45, STYRON A-200, AND NDR-359 IN BIS(2-CHLOROETHYL) ETHER, IN NITROBENZENE AND IN BIS(2-CHLOROETHYL) SULPHIDE

Solvent	% Iron salt	Bottles: Initial viscosity	Bottles: Final viscosity	Bombs
(a) 10% Gelva V-45				
Bis(2-chlorethyl) ether	Ferric			
	0.1	3.6	Gel 5 days	Gel 2 days
	0.01	3.3	Gel 38 days	Gel 4 days
	0.001	3.5	0.5 170 days	No gel 163 days
	0.0	3.5	0.5 170 days	—
	Ferrous			
	0.1	3.5	Gel 13 days	No gel 150 days
	0.01	3.5	Gel 22 days	No gel 150 days
	0.001	3.5	0.1 140 days	No gel 150 days
	0.0	3.5	0.5 140 days	—
Nitrobenzene	Ferric			
	0.25	—	Gel 12 hr.	—
	0.1	3.0	Gel 1 day	Gel 2 hr.
	0.01	4.4	Gel 2 days	Gel 13 hr.
	0.001	2.8	No gel 120 days	—
Bis(2-chloroethyl) sulphide	Ferric			
	1.0	—	Gel 1 day	Gel 1 day
	0.3	7.1	8.0 190 days	Gel 60 days
	0.1	6.6	8.5 190 days	Gel 82 days
	0.01	6.9	6.8 190 days	Gel 121 days
	0.001	7.0	7.0 190 days	Gel 150 days
	0.0	7.0	7.0 190 days	—
	Ferrous			
	0.1	6.7	8.0 150 days	Gel 130 days
	0.01	6.7	7.0 150 days	Gel 130 days
	0.001	6.7	6.5 150 days	Gel 130 days
	0.0	6.6	6.7 150 days	—
(b) 7.5% Styron A-200				
Bis(2-chloroethyl) ether	Ferric			
	0.1	3.0	Gel 38 days	—
	0.01	3.0	Gel 22 days	Gel 36 days
	0.001	3.0	0.5 140 days	No gel 140 days
	0.0	3.0	0.5 140 days	No gel 140 days
Nitrobenzene	Ferric			
	0.1	1.6	2.0 160 days	No gel 160 days
	0.01	3.0	2.0 160 days	No gel 160 days
	0.001	3.1	3.0 160 days	No gel 160 days
	0.0	3.1	3.0 160 days	No gel 160 days

TABLE VIII—*Concluded*

THE AGEING OF SOLUTIONS OF GELVA V-45, STYRON A-200, AND NDR-359 IN BIS(2-CHLOROETHYL) ETHER, IN NITROBENZENE AND IN BIS(2-CHLOROETHYL) SULPHIDE—*Concluded*

Solvent	% Iron salt	Bottles: Initial viscosity	Bottles: Final viscosity	Bombs
(c) 1% NDR-359				
Bis(2-chloroethyl) ether	Ferric			
	0.1	3.1	0.2 52 days	Gel 14 days
	0.01	12.0	0.4 52 days	No gel 175 days
	0.001	21.0	0.5 170 days	No gel 175 days
	0.0	20.0	0.5 170 days	—
Nitrobenzene	Ferric		Polymer	
	0.1	1.3	Sep. 104 days	Gel 16 days
	0.01	6.8	Stringy 175 days	No gel 175 days
	0.001	8.3	4.0 175 days	No gel 175 days
	0.0	9.7	5.0 175 days	No gel 175 days
Bis(2-chloroethyl) sulphide	Ferric			
	0.1	3.8	3.0 110 days	No gel 110 days
	0.01	10.3	4.0 110 days	No gel 110 days
	0.001	10.6	4.0 110 days	No gel 110 days
	0.0	11.5	4.5 110 days	No gel 110 days

For Gelva V-45 in bis(2-chloroethyl) ether and in nitrobenzene, concentrations of 0.01% or greater of ferric chloride cause gel formation. Similar solutions containing ferrous chloride and aged in bottles behave similarly. With bis(2-chloroethyl) sulphide as solvent the concentration of ferric chloride that will produce gels in solutions aged in the presence of air is of the order of 1%. At the same time, as little as 0.001% of either ferrous or ferric chloride causes gel formation in evacuated bombs.

Somewhat similar effects are noted in Parts (*b*) and (*c*) of Table VIII. Concentrations of ferric chloride of 0.01% or greater cause gel formation in solutions of Styron A-200 in bis(2-chloroethyl) ether. Little effect is observed in the solutions of Styron in nitrobenzene. This may be due in part to strong attraction between the polymer and the solvent, both being aromatic in character.

The failure of NDR-359 to form gels as readily as the other two polymers is due possibly to the low concentration of this material used. In some of the experiments the polymer appeared to separate out on ageing, leaving a solution of very low viscosity.

Whether a particular solution takes on gel characteristics or not appears to depend upon the degree of solvation of the polymer by the solvent. In nonsolvating solvents, gels are not to be expected. For example, a solution of Gelva V-45 in acetone containing 0.25% of ferric chloride was aged for 26

days at 60° C. in a sealed bomb. During this time, the viscosity increased from 17 to 21 centipoises. The polymer, after being recovered from the solution, was only partially soluble in benzene.

A similar solution with toluene as solvent was aged for $3\frac{1}{2}$ months at 60° C. The viscosity as measured in the Ubbelohde type viscometer increased from 23 to 36 centipoises. The original solution was Newtonian in flow properties, but after the ageing with ferric chloride showed deviations from Newtonian flow. This indicated the presence of gel structures.

Discussion

It is evident from the experimental data that small amounts of impurities may cause rather large variations in the viscosity of polymer solutions. Only small changes in viscosity are observed when solutions of the polymers in pure solvents are aged in evacuated bombs (Tables I and II). Oxygen from the air and iron in the form of a salt are probably not the only materials that can cause instability. The effect does not appear to be specific since it occurs in a variety of polymer–solvent systems. The magnitude of the change in viscosity is not the same in all cases, which is to be expected, since different weight concentrations of the polymers were used in preparing the solutions.

Changes in the viscosity of a solution containing macromolecules could be caused by variations in (*a*) the degree of solvation of the polymer, (*b*) the orientation or configuration of the macromolecules in solution, (*c*) the chemical nature of the polymer, and (*d*) the molecular weight of the polymer. It is hardly conceivable that either of the first two mechanisms could cause irreversible gel formation. In none of the work was a regular trend in the saponification value observed, for example, Tables II and VII. Besides, polystyrene cannot be hydrolysed, yet its behaviour was similar to that of the other two polymers (Table VIII). It seems then that alterations in the molecular weight of the dissolved polymer cause the changes in the viscosity of the thickened solutions. Certainly this is indicated by the similar trends of the viscosity of the thickened solutions and of the intrinsic viscosity of the recovered polymer (Table V). These changes in molecular weight may be accompanied by variations in the structure of the polymer. This is suggested by the trend in the k' value for the series in Table V.

It is not possible to determine the rates of the degradation or of the gel-forming reactions from the change in viscosity with time, because the viscosity property depends upon such factors as the shape of the macromolecules, the degree of solvation, and the conditions of measurement. Owing to the shape of the viscosity–molecular-weight diagrams for such systems, small increases or decreases in molecular weight at higher concentrations may cause large changes in the viscosity.

Little may be said concerning the actual mechanism of the reaction between the polymer and dissolved iron salts or oxygen, nor can reactions between the solvents and these added substances be excluded entirely. For example,

the degradation of the polymers in bis(2-chloroethyl) ether is greater than in the other solvents. This suggests the possibility of reaction of the impurities with bis(2-chloroethyl) ether, with the formation of compounds that also degrade the polymer. That the effects of iron salts and of oxygen may be interrelated is indicated by the fact that both ferrous and ferric chlorides cause gel formation in solutions of Gelva V-45 in bis(2-chloroethyl) sulphide in bombs, but not in bottles.

Oxygen appears to degrade the polymer chains while iron salts cause chain linking and frequently gel formation. The effect of iron seems to be chemical rather than catalytic, since a limiting concentration exists. In the case of bis(2-chloroethyl) ether and nitrobenzene this limit is between 0.01 and 0.001% as ferric chloride. The number average molecular weight of Gelva V-45 is approximately 140,000 (7), and, since approximately 10% by weight of the polymer was used in preparing the solutions, the ferric chloride and the polymer were present in nearly molar proportions. The gel-forming reaction is apparently quite irreversible, because several attempts to break the gels and recover the polymer were unsuccessful. Further speculation than this concerning the nature of the reaction between the iron salts and the polymer molecules appears unwarranted.

Acknowledgment

The authors wish to thank Dr. O. Maass for his help in obtaining financial assistance for this work and for his helpful interest in it.

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THE MOLECULAR WEIGHT OF SOME POLYVINYL ACETATES[1]

By R. McIntosh[2] and J. A. Morrison[3]

Abstract

The number average molecular weights of two series of polymer samples, recovered from aged solutions of polyvinyl acetate in bis(2-chloroethyl) ether, have been measured using a dynamic type osmometer. It is shown that these number average molecular weights change from sample to sample in a manner similar to the intrinsic viscosities of the recovered polymers. This confirms previous results, which suggested that the change in viscosity of solutions of high polymers on ageing was due primarily to changes in the molecular weight of the dissolved polymer. A method of evaluating a relative non-uniformity coefficient for the polymers is suggested.

Introduction

In another paper (10), the effect of iron salts and of oxygen in causing changes in the viscosity of solutions of high polymers has been described. For solutions of polyvinyl acetate in bis(2-chloroethyl) ether, it was shown that the intrinsic viscosity of the recovered polymer changed in a manner similar to the viscosity of the aged solutions. This fact suggested that the molecular weight of the polymer was altered during the ageing process. However, since the viscosity property of solutions may also depend upon factors other than molecular weight of the solute, it was desirable to have an absolute measure of the molecular weight. Number average molecular weights of the polymers recovered from two series of aged solutions have now been measured using an osmometer, and are reported here. These results establish that molecular weight changes do occur during the ageing of polymer solutions.

The modified form of the Staudinger equation, $[\eta] = KM^a$, has been used to correlate the results. The slopes a from the plots of the logarithm of $[\eta]$ against the logarithm of M_n for the two series of polymers differ from the slope previously found for polyvinyl acetates (3, 11). A difference in a for polystyrene polymerized at different temperatures has been reported by Alfrey, Bartovics, and Mark (1). From the observation that the μ (4) and k' (5) factors for the polymers differed, these authors have been led to the view that the change in a is brought about by changed internal architecture of the polymer molecules. In the present instance, the variation in k' is very small and the slopes of the π/c versus c plots are the same within experimental error. It appears then that the change in a is due to some other factor, possibly changes in the heterogeneity of the polymer samples. In Part II an attempt is made to evaluate a relative non-uniformity coefficient, β. The development is based upon the fact that the average molecular weight deter-

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Contribution from the Department of Chemistry, McGill University, Montreal, Que.
[2] *Honorary Sessional Lecturer, McGill University.*
[3] *Chemist, Department of National Defence.*

mined with an osmometer is a different average from that derived from the intrinsic viscosity.

Part I—Determination of Molecular Weights

Experimental

The osmometer was of the dynamic counter-pressure type. A full description of the cell and of the thermostat has been given (11), and no further comment is necessary here. The osmotic pressure measurements were made using dry acetone as solvent. The membranes were prepared by swelling No. 600 P.T. Cellophane (not waterproofed) in aqueous solutions of sodium hydroxide, followed by accommodation to the organic solvent. Two series of membranes were prepared, one series swollen in 1.5% sodium hydroxide, and the other in 4% sodium hydroxide. No difference in behaviour between the two types of membrane (except permeability to solvent) was observed. Both were completely impermeable to the polymer. Osmotic pressure values obtained with either type were concordant. Time lags in the establishment of equilibrium were short, and the slope of the π/c versus c plots was the same as that previously found for this type of membrane (11). No trend in osmotic pressure with time was observed. Refilling of the cell with solutions of the same concentration after an initial equilibrium value had been obtained was without effect.

The recovery of the polymers from aged solutions has been described (10). It is pertinent to emphasize again that changes in the chemical composition of the recovered polymers were within the limit of reproducibility of the analysis for acetate groups. Unfortunately, the quantitative comparison of the intrinsic viscosity and the number average molecular weight is subject to an uncertain error due to incomplete recovery of some of the polymer samples. Generally the yield on recovery was 98% or better, so that the error is probably not serious.

Results

The osmotic pressure data are given in Table I, and are represented graphically in Fig. 1. The π/c versus c plots for Samples 1 of both series were indistinguishable, and have been represented by a single line in Fig. 1. The polymer samples in Series I were recovered from solutions of polyvinyl acetate (Gelva V-45) in bis(2-chloroethyl) ether, aged in the presence of air at 60° C. The samples in Series II were recovered from solutions of Gelva V-45 in bis(2-chloroethyl) ether plus 0.003% ferric chloride, aged at 60° C. in glass bombs, which, after the solutions were degassed, were sealed at a pressure of 0.1 mm. of mercury. No peculiarities were observed in the determination of the osmotic pressures of Series I, but high values of osmotic pressure were observed near a concentration of 2.5 gm. per 100 cc. for the second sample of Series II, and at about 2.0 gm. per 100 cc. for the third sample. One additional sample of Series II was not investigated because of the narrowing concentration range over which it appeared feasible to work.

TABLE I

Osmotic pressure data of aged polymers

Series	Sample number	Membrane treatment	c*	π/c†	Limiting π/c at $c = 0$
I	1	1.5% NaOH	1.21	4.0_0	2.0_1
		1.5% NaOH	1.47	4.4_2	
		1.5% NaOH	1.58	4.7_7	
		1.5% NaOH	1.98	5.2_8	
		1.5% NaOH	2.36	5.9_3	
	2	4% NaOH	1.08	4.1_0	2.2_8
		4% NaOH	1.21	4.1_8	
		4% NaOH	1.46	4.7_5	
		4% NaOH	1.64	5.0_1	
	3	1.5% NaOH	1.00	4.1_0	2.4_3
		1.5% NaOH	1.56	5.0_5	
		1.5% NaOH	1.95	5.6_6	
	4	1.5% NaOH	0.97	4.4_6	2.7_5
		1.5% NaOH	0.99	4.2_8	
		1.5% NaOH	1.60	5.4_4	
		1.5% NaOH	1.78	5.7_0	
II	1	4% NaOH	1.17	3.8_5	2.0_1
		4% NaOH	1.57	4.5_7	
		4% NaOH	1.76	5.0_5	
		4% NaOH	2.04	5.4_5	
	2	1.5% NaOH	1.07	3.6_0	1.8_0
		4% NaOH	1.36	3.9_0	
		4% NaOH	1.19	3.8_0	
		4% NaOH	1.58	4.4_5	
		4% NaOH	1.82	4.6_5	
	3	1.5% NaOH	1.03	2.8_7	1.2_1
		1.5% NaOH	1.47	3.5_5	
		1.5% NaOH	1.95	4.3_5	
	4	1.5% NaOH	1.04	2.7_5	1.0_8
		1.5% NaOH	1.47	3.4_3	
		4% NaOH	1.77	3.8_8	

* *Concentration—grams of polymer/100 cc. of solution.*
† *π—osmotic pressure in centimetres of water.*

The derived data, $[\eta]$, k', M_n, and β are given in Table II. The values in Columns 3 to 6 have been reported (10), but are included again for convenience of comparison. The intrinsic viscosity of the first sample of Series II has been redetermined, the new value being 1.17 in place of 1.01 as given previously (10). The cause of the difference in intrinsic viscosity between Samples 1 of Series I and II is not clear. Qualitatively it has been observed that the addition of small amounts of ferric chloride brings about an immediate increase in the viscosity of polymer solutions.

The most important information in Table II is the changing value of M_n, which in both series follows a trend similar to that of the viscosity of the original solutions and of the intrinsic viscosity. It appears then that real changes in molecular weight occur when the polymer solutions are aged, and that these changes are the fundamental cause of the increase or decrease in viscosity. Certainly, the suggestion of Mead and Fuoss (9), that the

changes in viscosity are due to alterations in the form of the polymer in solution, is not an adequate explanation for the results.

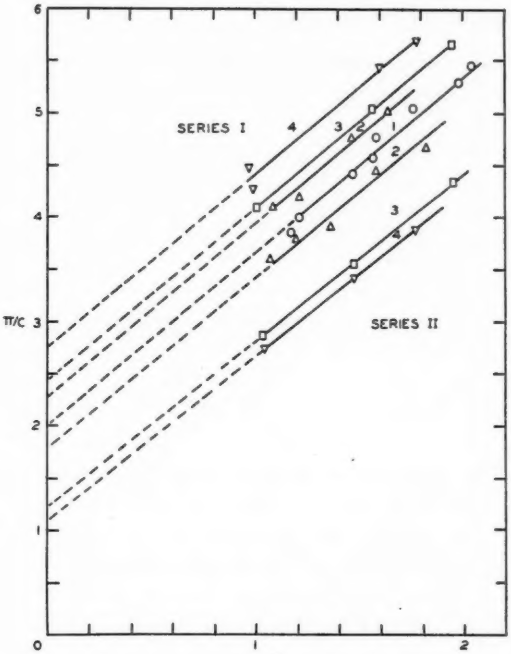

FIG. 1. *Plot of π/c versus c—data of Table I.*

TABLE II

VARIATION OF PROPERTIES OF SAMPLES WITH AGEING

Series	Original solution in bis(2-chloroethyl) ether						
	Sample number	Ageing time, days	Viscosity, poises	$[\eta]$	k'	M_n	β
I	1	0	3.70	1.07	0.34	128,000	2.1_4
	2	8	3.50	1.03	0.36	113,000	2.1_9
	3	87	3.25	0.98	0.36	105,000	2.1_8
	4	154	3.15	0.95	0.33	93,500	2.2_1
II	1	0	3.55	1.17	0.34	128,000	2.2_2
	2	1	5.45	1.24	0.37	143,000	2.2_1
	3	$2\frac{1}{2}$	8.70	1.59	0.38	220,000	2.1_9
	4	3	12.0	1.66	0.39	247,000	2.1_6

In Fig. 2 plots of log $[\eta]$ against log M_n for Series I and II are shown. The best straight lines through the experimental points have slopes of 0.38 and 0.54 for Series I and II respectively, as compared with 0.63 for unaged polyvinyl acetates (3, 11).

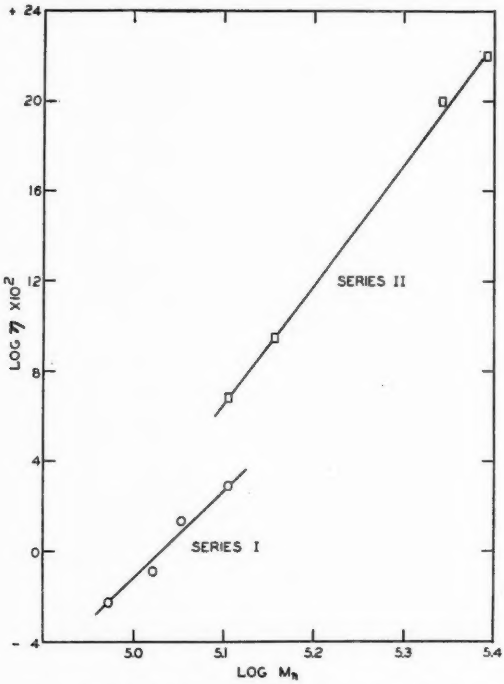

FIG. 2. *Plot of log* $[\eta]$ *versus log* M_n*—data of Table II.*

Part II—Non-Uniformity Coefficient

Theoretical

The intrinsic viscosity of a heterogeneous sample of polymer in terms of the intrinsic viscosity of each species is given by

$$[\eta] = \frac{\Sigma\, [\eta]_i w_i}{\Sigma\, w_i} \tag{1}$$

where $[\eta]_i$ = intrinsic viscosity of the ith species

w_i = weight of the ith species.

As has been pointed out by Mark (8, p. 56) and Lansing and Kraemer (6), if the Staudinger rule is applicable,

$$[\eta]_i = K_{st} M_i \tag{2}$$

where M_i = molecular weight of the ith species

K_{st} = Staudinger constant,

the definition of intrinsic viscosity in Equation (1) states that the intrinsic viscosity is proportional to the weight average molecular weight. Recently the Staudinger rule has been replaced by the relation

$$[\eta]_i = KM_i^a \tag{3}$$

probably first suggested by Mark (7, p. 103) and verified since by Houwink (3) and Flory (2).

Substituting Equation (3) into Equation (1) yields

$$[\eta] = \frac{\Sigma KM_i^a w_i}{\Sigma w_i} = \frac{K\Sigma M_i^{1+a} n_i}{\Sigma M_i n_i} \tag{4}$$

where n_i = number of molecules of the ith species.

The number average molecular weight measured by the limiting osmotic pressure method is given by

$$M_n = \frac{\Sigma M_i n_i}{\Sigma n_i} \tag{5}$$

To evaluate the two averages a distribution function relating the number of molecules of given molecular weight to the molecular weight must be assumed. In so doing, the summations are replaced by integrations, but since the increments of molecular weight are small compared with the molecular weight, the error introduced is probably very small. It is desirable to choose a distribution function that has a single maximum and represents substantially zero numbers of molecules of very low molecular weight and of very high molecular weight. Theoretically there are probably several functions that could be used, but the one adopted here is the logarithmic distribution, which has been used by Lansing and Kraemer (6) in the form

$$\frac{dn}{N} = \frac{I}{\sqrt{\pi}} e^{-y^2} dy \tag{6}$$

where $y = \dfrac{1}{\beta} \ln \dfrac{M}{M_0}$

dn = number of molecules between y and $y + dy$

N = total number of molecules.

M_0 and β may be considered as parameters of the distribution function. M_0 is the value of M corresponding to the maximum value of the tangent to the distribution curve, while β is defined as the non-uniformity coefficient. For homogeneous materials β is zero, and for heterogeneous materials it has a positive value.

Introducing the distribution function Equation (6) into Equations (4) and (5),

$$[\eta] = \frac{\dfrac{2NK}{\sqrt{\pi}}\displaystyle\int_0^{\infty} M^{1+a}\, e^{-y^2}dy}{\dfrac{2N}{\sqrt{\pi}}\displaystyle\int_0^{\infty} Me^{-y^2}dy} \tag{7}$$

$$M_n = \frac{\dfrac{2N}{\sqrt{\pi}}\displaystyle\int_0^{\infty} Me^{-y^2}dy}{N} \tag{8}$$

whence,

$$[\eta] = K\, M_0^a e^{\beta^2\left[\left(\frac{1+a}{2}\right)^2 - \frac{1}{4}\right]} \tag{9}$$

$$M_n = M_0\, e^{\frac{\beta^2}{4}} \tag{10}$$

Eliminating M_0 between Equations (9) and (10) gives

$$[\eta] = M_n{}^a K e^{\frac{\beta^2}{4}(1+a)a} \tag{11}$$

or

$$\ln\,[\eta] = a \ln M_n + \ln K + \frac{\beta^2}{4}(1+a)a \tag{12}$$

A plot of log $[\eta]$ against M_n will yield a straight line either if the polymers are homogeneous and β is zero, or if the polymers are heterogeneous and β is constant or else varies linearly with M_n. Relative changes of β, brought about by any reactions of the polymer where the molecular weight alone is altered, may be evaluated by the measurement of $[\eta]$ and M_n. The intercepts of the straight lines will depend upon β, and therefore the constant K cannot be determined with heterogeneous polymers. In the present instance, an arbitrary value must be chosen for K.

Results

In the calculation of β for the polymer samples in Series I and II, a was taken as 0.63 (11), and a value of 2.0×10^{-4} was selected arbitrarily for K. The values of β so determined are given in the last column of Table II. The change in β in either series is small, but qualitatively one would expect the trends that are observed. For Series I, if the degradation of each species is not complete, an extension of the molecular weight range in the sample would be expected. For Series II, a decrease in the degree of heterogeneity could be caused by a slightly greater rate of reaction of the lower molecular weight species.

However, the possible errors in the values of M_n may make meaningless the apparent changes in β. The errors in M_n are due principally to the long extrapolation of the π/c versus c plots that is necessary with the type of osmotic cell used. In addition, as has been pointed out, the quantitative comparison of the intrinsic viscosity and the number average molecular weight is subject to error due to incomplete recovery of the samples of polymer from the aged solutions.

Acknowledgment

The authors wish to express their thanks to Dr. O. Maass for his interest in this work and for arranging financial assistance.

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PREPARATION OF PICRYL CHLORIDE[1]

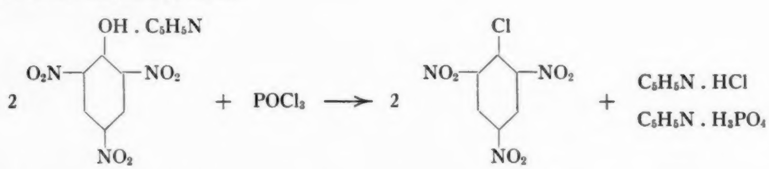
By Raymond Boyer[2], E. Y. Spencer[3], and George F. Wright[4]

Abstract

Picryl chloride can be prepared from pyridine picrate and either phosphorus oxychloride or phosgene in 97 to 100% yield. The pyridine used in this process is recoverable as its picrate and thus acts as a non-expended carrier during repeated preparations. Two of the chlorine atoms react in phosphorus oxychloride while only one in phosgene furnishes picryl chloride. The latter acid chloride is, however, more economical in use owing to its lower cost and molecular weight.

Picryl chloride can be prepared from one mole picric acid and two moles phosphorus pentachloride (1), but in our hands the yield was only 55% of the theoretical. The vigour of the reaction seemed to cause tar formation and to be potentially dangerous on the large scale. We modified Jackson and Gazzolo's procedure by addition of five moles of thionyl chloride and thus were able to carry out the reaction smoothly under reflux to give a 70% yield. The thionyl chloride evidently acted only as a solvent, since the use of a catalytic amount of phosphorus pentachloride in this solvent yielded no picryl chloride from picric acid. Sulphuryl chloride, phosphorus trichloride, and chlorosulphonic acid were likewise ineffective. None of these substances became reactive when catalytic amounts of benzoyl peroxide were added.

Phosphorus oxychloride also was unreactive toward picric acid alone, but we found that it reacted smoothly with pyridine picrate. Fifteen minutes' reflux in benzene solution gave a yield of good quality picryl chloride which was 98% of theoretical. Although two of the chlorine atoms in phosphorus oxychloride are available for picryl chloride formation the use of 1 : 2 ratio led to an impure product.



Practically, we have used about 0.7 moles of phosphorus oxychloride per mole of salt in order to obtain a 98% yield of good picryl chloride melting at 79° to 81° C.

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Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont.

[2] *Visitor under War Technical and Scientific Development Committee, National Research Council of Canada, June-September, 1940.*

[3] *Holder of Studentship under the National Research Council of Canada, 1940–41; present address: University of Saskatchewan.*

[4] *Professor of Chemistry.*

In the event that a considerable quantity of picryl chloride were needed, the process could be made both convenient and economical. The soluble pyridine salts, which remain in the aqueous liquors used to wash the benzene solution, may be precipitated by addition of picric acid to the warm aqueous liquors. This regenerated pyridine picrate (93% recovery) is entirely adequate for a subsequent preparation.

The reaction between picric acid and phosphorus pentachloride yields phosphorus oxychloride. Since both of these phosphorus halides are priced the same in quantity lots, it may be calculated stoichiometrically that a slight advantage in quantity manufacture would result by initial use of phosphorus pentachloride on picric acid, followed by recovery of the phosphorus oxychloride for subsequent utilization with pyridine picrate. This stepwise operation would be necessitated by the fact that phosphorus pentachloride (as well as phosphorus trichloride, sulphuryl chloride, and chlorosulphonic acid) will not react with pyridine picrate, although it will react with picric acid.

All such speculation respecting economical production of picryl chloride from the phosphorus halides was, however, cut short by the discovery that phosgene, which was unreactive toward picric acid at 100° C. during three hours' contact, reacted quantitatively with pyridine picrate. The salt was treated in an autoclave for two hours at 56° C. with 50% or greater excess of phosgene to give a 100% yield of crude picryl chloride melting at 79° to 80° C. This crude was the residue obtained by atmospheric evaporation of the recoverable phosgene followed by aqueous wash to remove the pyridine hydrochloride. Although only one of the chlorine atoms in phosgene is available for picryl chloride formation, the chloride affords a cost advantage of at least 20% over the process using phosphorus halides.

Most of our work was carried out in low pressure autoclave equipment, but it was found that 97% yield could be effected by condensing phosgene into pyridine picrate at 0° C. After one-half hour, the excess of phosgene was evaporated at room temperature and the residue washed with water to remove the recoverable pyridine hydrochloride.

The pyridine picrate used initially in this process was prepared in 98% yield by combination of the ingredients in ethanol. The salt, melting at 166° C., was much easier to filter than that prepared in aqueous solution from equivalent amounts of hot aqueous sodium picrate and pyridine hydrochloride. The melting point of this cheesy precipitate, 242° C., was unaffected by resolution and recrystallization from its own mother liquors or from ethanol, but when crystallized from pure water it melted at 166° C. When technical pyridine (average molecular weight of 107 in contrast to pyridine of 79) was used instead of pure pyridine for preparation of the salt, the precipitate melted at 88° to 153° C. as might be expected of a mixture of salts. This impure picric acid salt was, however, equally effective in picryl chloride preparation with that derived from pure pyridine.

The recovery of pyridine from the products prepared from phosphorus oxychloride was effected by precipitating calcium phosphate from the aqueous

liquors used to wash the benzene solution of picryl chloride. After this treatment with an excess of lime, picric acid was added to the hot stirred filtrate until precipitation of pyridine picrate was complete. The lime treatment was, of course, not necessary when phosgene was used as the acid chloride. In either case the pyridine picrate was thoroughly air-dried before re-use.

Although the crude products from these preparations are not pure picryl chloride, which melts at 83° C., they are adequate for many uses. Thus this crude picryl chloride could be converted in 99% yield to N-methylpicramide, which in turn was pure enough that it could be converted in 97% yield to pure tetryl.

Experimental*

Preparation of Pyridine Picrate

Method 1.—To a solution of 22.9 gm. (0.1 mole) picric acid in 200 cc. of hot 95% ethanol was added 7.9 gm. (0.1 mole) of pyridine. A 98% yield (30.1 gm.) was filtered off the cooled solution. The salt melted at 166° C.

Method 2.—To a solution of 22.9 gm. (0.1 mole) of picric acid dissolved in 200 cc. of hot 2% aqueous sodium hydroxide was added 7.9 gm. (0.1 mole) of pyridine in 28.6 cc. of dilute hydrochloric acid. A cheesy precipitate, difficult to filter, was obtained on cooling. It weighed 28.1 gm. (91% of theoretical) and melted at 242° C. This melting point was unchanged after crystallization from ethanol or from the precipitating liquors but water recrystallization converted it to the ordinary pyridine picrate melting at 166° C.

Picryl Chloride from Phosphorus Oxychloride

One mole (308 gm.) of dry pyridine picrate was boiled for 15 min. under reflux with 0.67 mole (103 gm.) of phosphorus oxychloride in 250 cc. benzene. Both the precipitated oil and the benzene layer were washed several times with hot water. The benzene solution on evaporation yielded 73% of the theoretical amount of picryl chloride while the residue from the precipitated oil constituted 25% of the theoretical yield. The total (98% yield) picryl chloride melted at 79° to 81° C.

The aqueous washing liquors were treated with an excess of hydrated lime to remove phosphate. After filtration the solution was heated to 70° C. and stirred while one mole (229 gm.) of picric acid was added slowly to insure solution. The pyridine picrate that precipitated completely on cooling melted at 166° C. and weighed 298 gm. or 97% of theoretical. This was air-dried before re-use together with the evaporated benzene.

Picryl Chloride from Phosgene

Into one mole (308 gm.) of dry pyridine picrate in a light iron pressure vessel or bomb tube was poured or condensed 1.5 moles (148.5 gm.) of commercial phosgene. After two hours or less at 56° C. the pressure was released to distil off the excess phosgene. The remainder was blown with air to remove

All melting points are corrected.

last traces of poisonous gas and was then ground in a mortar with three 500 cc. portions of water at 70° C. The remaining picryl chloride weighed 247 gm. (100% yield) and melted at 78° to 79.5° C.

The combined aqueous wash liquors were heated to 70° C. and stirred while 1 mole (229 gm.) of picric acid was added slowly. After cooling to complete precipitation the pyridine picrate was filtered off and air-dried to weigh 287 gm. or 93% of the amount originally added. Either quinoline or the mixture of pyridine, picolines, and lutidines known as "technical pyridine" works as satisfactorily except that filtration of the recovered pyridine salts is slightly more difficult.

This method of picryl chloride preparation may be varied by eliminating the heating period at 56° C. After the phosgene was poured or condensed into the pyridine picrate at 0° C., the mixture was let stand at this temperature for 30 min. and then warmed to 25° C. to remove the phosgene. The yield of picryl chloride, m.p. 78° to 79° C., from an otherwise identical procedure was 96.7% of theoretical. The yield was, however, decreased to 50% or less when gaseous phosgene was passed over thin layers of pyridine picrate either at 25° or 55° C. for 30 min.

Preparation of N-methylpicramide

The method of van Romburgh (2) was followed by adding 0.024 mole (0.74 gm.) of methylamine in 4 cc. methanol to 0.01 mole (2.47 gm.) of crude picryl chloride, m.p. 78° to 79.5°, in 3 cc. methanol at 20° C. The crystals were filtered off and washed once with methanol. The combined methanolic solutions were evaporated and the crystal crop recrystallized from benzene. In this manner a 99.2% yield (2.40 gm.) of N-methylpicramide, m.p. 110° to 110.5° C., was obtained.

Preparation of N-methyl-N-nitropicramide (Tetryl)

Treatment of 0.0025 mole (0.61 gm.) of N-methylpicramide, m.p. 110° to 110.5°, with 0.06 mole (4 cc.) of 70% nitric acid, followed by evaporation on the steam-bath gave a yellow residue. When this was water-washed and dried it represented a 97.0 yield of tetryl melting at 128° to 129° C.

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PREPARATION OF PICRAMIDE[1]

By E. Y. Spencer[2] and George F. Wright[3]

Abstract

The method of Kym for conversion of phenols into aromatic amines has been applied to picric acid. An 88% yield of picramide has been obtained by adjusting the reaction temperature to 173° C., the molar urea : picric acid ratio to 3 : 1, and the reaction time to 36 hr.

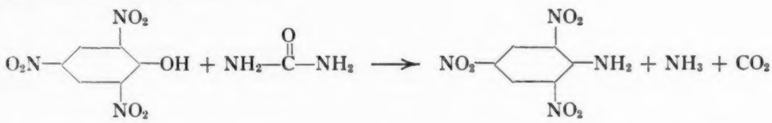
In connection with the preparation of tetranitrobenzene (2), we required a cheap, plentiful, and safe method for obtaining the necessary picramide. The method of Merz and Ris (4), which involves the action of 35% ammonia on nitrophenols to give aminonitrobenzenes, gave a charcoal-like product with picric acid after 16 hr. at 160° to 170° C. A control experiment involving picramide instead of picric acid under the same conditions showed that 88% of the picramide was recoverable and therefore would not have been destroyed under this reaction environment. Similarly no picramide could be obtained from picric acid and zinc chloride ammoniate ($ZnCl_2 . 2NH_3$) at 155° C., although a comparable experiment with picramide showed no degradation.

Kym (3) has reported that nitrophenols can be converted to aminonitrobenzenes by heating the phenol with urea. Thus he obtained a 75% yield of 2,4-dinitroaniline from one part of 2,4-dinitrophenol and three parts (9.2 moles) of urea at 208° C. for eight hours. We found that this method was applicable to the preparation of picramide.

Our first experiments were carried out for seven hours at 155° C. using Kym's 9.2 molar ratio of urea to picric acid. The 12% yield could be increased to 26% by increasing the reaction time to 16 hr. A further yield increase to 45% was effected by raising the temperature to 173° C. and this was augmented to 67% by reducing the molar urea–picric acid ratio to 4.5.

The reaction produces ammonia and ammonium carbonate as might be expected from Equation (I),

I



and on this basis an excess of urea would seem to be unnecessary. However, a water and acetone-insoluble by-product is formed which must arise by decomposition of the urea. This alternative consumption of urea may account for

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Contribution from Department of Chemistry, University of Toronto, Toronto, Ont.

[2] *Holder of Studentship under the National Research Council of Canada, 1940–1941. Present address: University of Saskatchewan.*

[3] *Professor of Chemistry.*

the fact that a low yield, chiefly ammonium picrate, was obtained when equimolar quantities of picric acid and urea were heated 16 hr. at 173° C. Two moles of urea per mole of picric acid was still not sufficient to supply reagent for both main and side-reactions, since a yield of 15% picramide was optimum under these conditions. The use of three moles of urea seemed, however, to supply an adequate excess.

This 3 : 1 molar ratio of urea to picric acid produced 73% of picramide in 13 hr. Time of reaction, and not further excess of urea, was shown to be the limiting yield factor by evaporating to dryness the water-washing liquor from this latter picramide yield and then reheating aliquots of the residue for 24 hr. longer, with and without additional urea. A further 12% yield was obtained in either case. This finding was substantiated by a complete experiment wherein three moles of urea per mole of picric acid was heated 36 hr. at 173° C. to give an 88% yield of picramide melting at 187° to 188° C. A slightly higher (91%) yield of poorer product (m.p. 185° to 189° C.) was obtained at a reaction temperature of 183° C.

The fate of the reagents is shown in the following capitulation of this latter experiment.

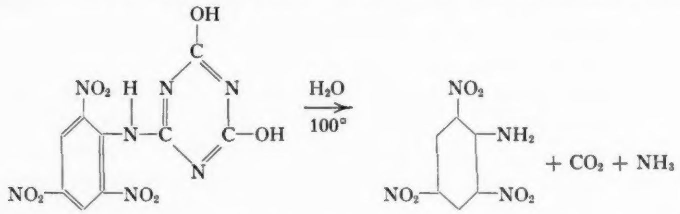
	Grams	Moles	Weight, gm.	Moles
Reagents:				
(Picric acid)	229	1		
(Urea)	180	3		
Products:				
Water soluble (urea)			31.8	0.53
Sublimate (ammonium carbonate by titration)			70.2	0.73
Gas evolved (ammonia by titration)			5.7	0.33
Picramide (m.p 185°–189°)			207.7	0.91
Acetone-insoluble (as derivatives of cyanic acid)			63.2	1.47(as cyanic acid)
(as "bound" picramide)			15.8	0.07
Total recovered			394.4	

This 96% material recovery affords some insight into the fate of the urea and the course of the reaction, although a thorough knowledge could be realized only by complete analysis of the acetone-insoluble material.

This analysis is not complete. Extraction with boiling water yields 25% of its weight as cyanuric acid. When the remainder is boiled with 600 parts of water, ammonia is produced, together with a small amount of cyanuric acid. The poorly crystalline material which precipitates on cooling represents 23% of the total; this material yielded 90% of its weight as pure picramide when it was extracted with acetone. Neither picric acid, melamine nor biuret could be detected.

This indicates that about 75% of the acetone-insoluble material is a condensation product of picrylurea. Although the solubility of the acetone-insoluble material in alkali would indicate that this might be picrylammelide,

II



the material must necessarily be more complex in order to account for the limited weight of picramide that is recovered after its decomposition. Further speculation seems fruitless until some means can be found to characterize further this intractable material. It must at present be considered a material bound by urea decomposition products from which, by boiling, sufficient picramide can be recovered to bring the total yield of the latter substance to 98% of the theoretical amount. It probably is significant that with increasing ratio of urea to picric acid the yield of acetone-soluble (free) picramide *decreased* while the amount of acetone-insoluble material increased.

The material balance (1 picramide: 1.79 NH_3 : 0.73 CO_2) shows, either that part of the carbon dioxide product according to Equation (I) is utilized in urea condensation, or, more probably, that the reaction follows an alternate course:

III $$ROH + NH_2CONH_2 \longrightarrow RNH_2 + HOOCNH_2$$

IV $$HOOCNH_2 \longrightarrow H_2O + HCNO$$

while the ammonia, ammonium carbonate, and the remainder of the cyanic acid involved in the acetone-insoluble material are derived by decomposition of urea. Such formulations are, of course, subject to urea decomposition equilibria at temperatures below 200° (5), nor is the intermediate formation of urea picrate and picrylurea excluded.

Experimental*

Picramide

One mole of picric acid melting at 120° to 121° C (229 gm.) was mixed with three moles (180 gm.) of technical urea in a 1 litre distilling flask equipped with a side-arm of 20 mm. diameter. The effluent from the receiver was passed through standard acid. At the end of the experiment both the ammonium carbonate in the receiver and the ammonia absorbed in the acid were estimated independently. The reaction flask neck was equipped with a thermometer with bulb immersed in the reagents.

* *Melting points corrected against known standards.*

The reaction flask was suspended with its equator 4 to 5 inches below the lip of a 3 litre beaker. Above the equator was coiled copper tubing to act as a condenser, and the flask neck was surrounded with a loosely fitting lid to eliminate bath losses owing to draughts. The beaker was filled about 1 inch in depth with *o*-dichlorobenzene (b.p. 183° C.) or a mixture of this with *p*-dichlorobenzene in case a lower temperature such as 173° C. was desired. A bare nichrome heating coil (250 watt) was immersed in the dichlorobenzene.

After 36 hr. reflux the flask content was removed from the flask with 1500 cc. water at 40° C. The aqueous washings were concentrated and the amount of recovered pure urea (m.p. 130° to 165° C.) was determined in this concentrate by dry weight. The water-insoluble portion of the reaction mixture was eluted with 2,000 cc. acetone in a Soxhlet extractor. The picramide was recovered from this acetone solution by evaporation of the solvent to weigh 207.7 gm. (91% of theoretical) and melt at 185° to 189° C. Further purification from acetone raised this melting point to 188° to 189° C. with a recovery of 88%.

The brown acetone-insoluble product dissolved, for the most part, slowly in 20 to 30% alkali to yield, after 20 hr., the insoluble crystalline trisodium cyanurate. Alternatively 25% of the acetone-insoluble material could be recovered as cyanuric acid by five-minute extraction with 25 parts of boiling water. This compound was identified by its crystal form, its loss of solvate water on heating to 56° (15 mm.) and by the titrimetric conversion of its trisodium salt to the disodium salt using phenolphthalein as indicator (1).

A 2.18 gm. aliquot of the cyanuric acid-free acetone-insoluble material was boiled one hour with 600 parts of water and filtered hot. The precipitate that appeared on cooling was filtered off, dried, and 0.5 gm. was boiled for 30 min. with 25 ml. acetone. The filtered solution was evaporated under 15 mm. to yield 0.43 gm. of picramide, m.p. 188° to 189° C. This melting point was not depressed by admixture of the product with an authentic sample.

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CHLORINATION BY AQUEOUS SODIUM HYPOCHLORITE[1]

By C. Y. Hopkins[2] and Mary J. Chisholm[2]

Abstract

New instances of nuclear chlorination of benzene derivatives by the action of cold aqueous sodium hypochlorite are reported. The reaction gives good yields of monochloro derivatives when the orientation is favourable.

Introduction

It is known that certain cyclic compounds can be halogenated by the action of aqueous hypohalites. Chlorination of benzoic acid by aqueous sodium hypochlorite was studied by Smith (12). He obtained a mixture of the three isomeric monochlorobenzoic acids as well as some dichloro acid. Salicylic acid undergoes chlorination in the same way, yielding a mixture from which some monochloro-salicylic acid can be isolated (4).

Nuclear chlorinated products have been prepared in the present work from various substituted benzoic acids, arylacetic acids, aryloxyacetic acids, and arylaldehydes, using sodium hypochlorite as the reagent. The results indicate that this method of halogenation is more widely applicable than previously supposed.

The procedure is extremely simple. The substance is dissolved or suspended in dilute alkali and mixed with sodium hypochlorite solution. It is left for an hour at ordinary temperature with occasional stirring. The product is then removed.

Certain substances, in which the orientation is most favourable, give monochloro derivatives in almost theoretical yield. These include vanillin, anisic acid, and piperonylacetic acid. The position taken up by halogen is the same as in ordinary non-aqueous chlorination. There is apparently no oxidation of the aldehyde group in the reaction with vanillin.

Experimental

A solution containing one mole of sodium hypochlorite per litre was prepared as the reagent (6). A suspension of calcium hypochlorite may be used but gives slightly lower yields. The general method of chlorination is illustrated by the reaction of sodium hypochlorite solution with anisic acid as follows:

Anisic acid (3.8 gm., 1/40 mole) was dissolved in 150 cc. of water and 25 cc. of 4% sodium hydroxide solution. It was cooled to 20° C., and mixed with 50 cc. (1/20 mole) of sodium hypochlorite solution. The temperature was

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[2] *Chemist.*

maintained at 20° C. for one hour with occasional stirring. Upon acidifying, a precipitate of almost pure 3-chloroanisic acid was obtained. The yield was 3.9 gm. (80% of theory). After one crystallization from toluene it melted at 215° C.

The experiments are summarized in Table I.

TABLE I

CHLORINATION PRODUCTS

Starting material	Moles NaOCl	Substitution product	Yield, %	M.p. after recrystallizing, °C.*	Reference
Anisic acid	2	3-chloro-	80	215	(2)
Vanillic acid	2	5-chloro-	85	242 to 244	(10)
p-Hydroxybenzoic acid	2	3,5-dichloro-	50	256 to 258	(5)
m-Methoxybenzoic acid	2	6-chloro-	60	170 to 171	(7)
2-Hydroxy-4-acetoxy-benzoic acid	2	5-chloro-	40	176 to 177	
Piperonylacetic acid	2	6-chloro-	80	177 to 178	(8)
Anisylacetic acid	1	3-chloro-	50	94 to 95	(8)
Vanillin	1.5	5-chloro-	90	164 to 165	(9)
Piperonal	1 or 2	6-chloro-	Poor	106 to 110	(13)
2,4-Dihydroxy-benzaldehyde	1.3	5-chloro-	80	156 to 157	(1, 3)
Phenoxyacetic acid	4	2,4-dichloro-	75	138 to 139	
2-Chlorophenoxy-acetic acid	2	2,4-dichloro-	80	138 to 139	
2-Methylphenoxy-acetic acid	1	4-chloro-	85	118 to 119	

* *Melting points are not corrected.*

Notes on the Products

5-Chlorovanillic acid.—This product was also made by chlorinating vanillic acid in chloroform by gaseous chlorine. It is considered to be 5-chlorovanillic acid since bromination by the same procedure is known to give 5-bromovanillic acid. The melting point agrees with that given by Raiford and Potter (10) for 5-chlorovanillic acid prepared from 5-chlorovanillin. The substance is readily soluble in ethanol and ether, slightly soluble in toluene, and insoluble in chloroform and hexane.

Chlorination of p-hydroxybenzoic acid.—A monochloro derivative could not readily be isolated.

2-Hydroxy-4-acetoxy-5-chlorobenzoic acid.—β-Resorcylic acid itself did not react normally with sodium hypochlorite, but monoacetyl-β-resorcylic acid gave the monochloro derivative without difficulty, m.p. 176° to 177° C. This substance has not been reported hitherto. Upon hydrolysis, it yielded 2,4-dihydroxy-5-chlorobenzoic acid, m.p. 218° C. (11).

6-Chloropiperonylacetic acid.—Found: Cl, 16.34, 16.61%. Calc. for $C_9H_7O_4Cl$: Cl, 16.55%. It did not depress the melting point of an authentic sample prepared by the method of Naik and Wheeler (8). The substance is

readily soluble in alcohol, ether, and acetic acid, and is moderately soluble in benzene and chloroform. It is insoluble in hexane.

5-Chlorovanillin.—This substance was identified by mixed melting point with an authentic sample prepared by the method of Raiford and Lichty (9). It crystallizes from water in small plates. It is soluble in alcohol, moderately soluble in benzene, and sparingly soluble in water.

6-Chloropiperonal.—Piperonal gave a mixture of chlorinated products from which 6-chloropiperonal was isolated in poor yield, m.p. 106° to 110° C.

5-Chloro-2,4-dihydroxybenzaldehyde.—This product is evidently the monochloro derivative prepared by Gattermann (3), m.p. 157° C. The position of the chlorine group was established by Chakravarti and Ghosh (1).

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THE FATTY ACIDS OF HARE'S-EAR MUSTARD SEED OIL[1]

By C. Y. Hopkins[2]

Abstract

The fatty oil of hare's-ear mustard seed (*Conringia orientalis* L.) was examined. Constants of the oil were determined and a partial separation of the fatty acids was carried out by the methyl ester fractionation method. Palmitic, oleic, linoleic, eicosenoic, erucic, and lignoceric acids were identified. Erucic acid was found to be present in largest amount. The oil resembles rapeseed and other Cruciferae seed oils in this respect. The content of eicosenoic acid is estimated to be not more than 12% of the total fatty acids.

Introduction

The screenings from grain grown in Western Canada contain quantities of weed seeds of the Cruciferae. During a study of the economic utilization of screenings, the fatty oils of a number of these seeds were examined and it was found that the oil of hare's-ear mustard seed (*Conringia orientalis* L. (Dumort.))* closely resembles rapeseed oil in its physical characteristics. The examination of the fatty acids of hare's-ear mustard seed oil was then undertaken.

Experimental

The seed was obtained from a commercial sample of grain screenings. It was separated from the mixture of weed seeds therein by means of a machine specially constructed for the purpose in the laboratory. Small amounts of chaff and hulls were removed by aspiration. Three kilos of the seed was ground in a small roller mill and extracted with petroleum ether in an apparatus of the Soxhlet type. The yield of oil was 29.5% of the air-dry material. It was bright yellow in colour and had the characteristics shown in Table I.

TABLE I

Characteristics of the oil

Property	Hare's-ear mustard seed oil	Rapeseed oil (8)
Iodine number	107	98–106
Saponification number	173	170–178
Sp. gr. 15° C.	0.9135	0.914–0.916
Refractive index, 25° C.	1.4714	1.471

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[2] *Chemist.*

* *The plant is also known under the following names: Brassica orientalis, Brassica perfoliata, Erysimum orientale, Erysimum perfoliata, Conringia perfoliata.*

The quantitative examination of the fatty acids was carried out according to the general method of Hilditch and co-workers (6). The oil was saponified by means of alcoholic potash, and the resulting anhydrous soap was mixed with pure sand and extracted thoroughly with acetone to remove the non-saponifiable portion. The residual soap was converted into the corresponding mixed fatty acids and these in turn were treated with lead acetate in boiling alcohol to form the lead salts. The latter were separated into three groups as described by Hilditch, Riley, and Vidyarthi (7), viz., those insoluble both in alcohol and in ether (*S*), those insoluble in alcohol but soluble in ether (*E*), and those soluble in alcohol (*A*).

The three groups of lead salts were converted separately to fatty acids. Each group of acids was esterified with methyl alcohol.

The esters were fractionally distilled *in vacuo* using a heated column with metallic packing, an oil-pump maintaining a vacuum of 2.5 mm. or less and a receiving device permitting uninterrupted distillation.

Examination of S Esters

The result of the fractionation of the *S* esters is shown in Table II.

TABLE II

FRACTIONATION OF *S* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*S*1	-123	2.5	14.2	1.4292
*S*2	123–150	11.0	17.1	1.4416
*S*3	150–181	7.8	63.6	1.4503
*S*4	181–200	26.6	70.9	1.4550
*S*5	200–205	20.0	70.4	1.4548
*S*6	Residue	54.8	63.7	—
		122.7		

Fraction *S*1 appeared to consist chiefly of non-acidic matter. Neither palmitic nor oleic acid could be detected.

Fraction *S*2 was saponified and the acids were recrystallized from alcohol. They yielded palmitic acid in quantity, m.p. 61° to 62° C.* (alone and mixed with an authentic specimen), neutralization equivalent, 257 (palmitic acid, 256). The acids from the mother liquor were treated with alkaline permanganate solution by the method of Lapworth and Mottram (9) in order to hydroxylate the unsaturated acids. After removal of palmitic acid by solution in hexane, the dihydroxy acids were recrystallized from ethyl acetate, and proved to consist chiefly of a dihydroxystearic acid, m.p. 116° to 117° C. It is more soluble in ethyl acetate and in ether than is the ordinary 9, 10-dihydroxystearic acid and is evidently produced from the same oleic acid found

* *Melting points are not corrected.*

by Hilditch and others in rapeseed oil (7). The dihydroxystearic acid reported by Hilditch melted at 117° to 118° C. Its constitution was not established definitely.

In addition, a very small amount of a second dihydroxy acid melting indefinitely at 125° C. was obtained, and this is presumably the dihydroxystearic acid (m.p. 132° C.) from ordinary 9 : 10 oleic acid. Linoleic acid was absent.

The acids from *S*3 were mainly unsaturated. After the usual oxidation, a small proportion of saturated acid melting at 54° to 56° C. was obtained. The hydroxylated acids were extracted with dry ether in a Soxhlet. The extract yielded the dihydroxystearic acid, m.p. 115° to 116° C., in quantity, and the residue had a melting point of 121° to 122° C., indicating the presence of the ordinary 9 : 10 oleic acid.

Fraction *S*4 was hydroxylated in the usual way and yielded a hydroxy acid that melted at 128° to 129° C. when recrystallized from ethyl acetate. This acid produced a depression in melting point when mixed with either 9, 10-dihydroxystearic acid or dihydroxybehenic acid. Its identification as dihydroxyeicosanoic acid is described in a subsequent paragraph. Lesser quantities of another unsaturated acid and of a saturated acid were indicated. Linoleic acid was absent.

The acids from *S*5 contained erucic acid, which gave dihydroxybehenic acid, m.p. 130° to 130.5° C. (alone and mixed with an authentic sample), and a saturated acid, m.p. 82° to 84° C., considered to be lignoceric acid.

The residue (*S*6) was assumed, from the analytical figures and analysis of the previous fraction, to contain only erucic and lignoceric acids.

Examination of E Esters

The *E* esters were fractionated in the manner described previously and the analysis of the various fractions was carried out in the same way as for the *S* esters.

The result of the fractionation is shown in Table III.

TABLE III

FRACTIONATION OF *E* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*E*1	90–127	1.6	42.7	1.4338
*E*2	127–168	5.9	52.4	1.4471
*E*3	168–171	33.5	111.5	1.4549
*E*4	171–174	19.9	118.8	1.4561
*E*5	174–176	16.5	103.9	1.4574
*E*6	176–184	12.6	92.7	1.4588
*E*7	184–188	43.5	82.6	1.4545
*E*8	188–193	14.6	77.9	1.4552
*E*9	193–198	43.7	73.3	1.4555
*E*10	Residue	51.1	70.8	—
		242.9		

Fraction *E*2, after saponifying and hydroxylating, yielded palmitic acid, m.p. 61° to 62° C. when recrystallized from alcohol. The hexane-insoluble hydroxy acids gave tetrahydroxystearic acid (from linoleic acid), m.p. 173° C., after recrystallizing from alcohol. There was also obtained a dihydroxy acid melting at 117° to 118° C., evidently from the same oleic acid described under *S*2.

Fraction *E*3 yielded the ordinary 9,10-dihydroxystearic acid, m.p. 128° to 130° C., alone and mixed with an authentic sample.

The acids from *E*5 were found to contain linoleic acid, identified as the tetrahydroxy derivative. Other hydroxy acids, not readily separable were obtained. There was little or no saturated acid.

The acids from *E*7, a large fraction in the C_{20} range, were examined in detail. A small proportion of linoleic acid was found. There was obtained a considerable quantity of dihydroxyeicosanoic acid, m.p. 129° to 130° C., as in *S*4.

There was also found, after hydroxylation, a hexane-soluble acid, or mixture of acids, which was unsaturated and melted at 46° to 48° C. This substance is described in a subsequent paragraph.

Fraction *E*8 contained no linoleic acid but was otherwise similar in composition to *E*7. Fraction *E*9 was found to be almost pure methyl erucate. Erucic acid, m.p. 32° to 34° C., was isolated and dihydroxybehenic acid was also prepared.

Examination of A Esters

The result of the fractionation of the *A* esters, the most unsaturated group, is shown in Table IV.

TABLE IV

FRACTIONATION OF *A* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*A*1	90–160	2.7	56.7	1.4507
*A*2	160–165	4.6	104.0	1.4571
*A*3	165–172	41.3	135.7	1.4572
*A*4	172–176	18.5	133.5	1.4590
*A*5	176–187	17.2	100.8	1.4572
*A*6	187–194	15.5	86.0	1.4558
*A*7	194–210	20.9	78.2	1.4560
*A*8	Residue	24.0	76.5	—
		144.7		

The acids from *A*2 yielded palmitic acid, m.p. 61° to 62°C. There was only a trace of saturated acid in *A*3. Fraction *A*4 contained much linoleic acid, obtained as tetrahydroxystearic acid, m.p. 172° C. Oleic acid is presumed to be present but it was difficult to purify the corresponding dihydroxy derivative.

Fraction *A*7 gave dihydroxybehenic acid (from erucic acid), m.p. 126° to 127° C. There was some indication of the presence of a doubly unsaturated acid, evidenced by the formation of a hydroxv derivative relatively insoluble in ethyl acetate.

A complete list of the acids that were identified is given in Table V.

TABLE V

IDENTIFICATION OF CONSTITUENT ACIDS

Chain length	Acid	Where found	Identified as	M.p. found, ° C.
C_{16}	Palmitic	*S*2, *E*2, *A*2	Palmitic acid	61– 62
C_{18}	Oleic	*S*2, *S*3, *E*2	Dihydroxystearic acid	116–117
				117–118
		*E*3	9,10-Dihydroxystearic acid	128–130
	Linoleic	*E*2, *E*5, *E*7, *A*4	Tetrahydroxystearic acid	173
C_{20}	Eicosenoic	*S*4, *E*7, *E*8	Dihydroxyeicosanoic acid	128–129
				129–130
C_{22}	Erucic	*S*5, *E*9, *A*7	Erucic acid	32– 34
			Dihydroxybehenic acid	130
C_{24}	Lignoceric	*S*5	Lignoceric acid	82– 84

The hexabromide test was applied to the original mixed fatty acids. The test showed that little or no linolenic acid is present. It was judged that the amount could not be more than 1% of the total fatty acids.

Dihydroxyeicosanoic Acid

Treatment of certain fractions of the fatty acids with cold alkaline permanganate solution resulted in the isolation by crystallization from ethyl acetate of a substance identified as dihydroxyeicosanoic acid.

The procedure was as follows: 5 gm. of a distilled fraction of the methyl esters was saponified and the solution was evaporated to a paste. The latter was dissolved in 3 litres of water, made neutral, and 5 gm. of sodium hydroxide added. The solution was kept at 15° C. while 400 cc. of 1% potassium permanganate solution was added with stirring. The mixture was stirred for 15 min. and was then decolorized by passing in sulphur dioxide. It was acidified by the addition of concentrated hydrochloric acid.

The white, flocculent precipitate was dried and extracted in a Soxhlet with hexane to remove saturated acids, then with dry ether to remove most of the dihydroxystearic acids. The remainder was recrystallized from ethyl acetate. In the case of the acids from *E*7, which gave the largest quantity of the product, the crystals melted at 129° to 130° C. The same substance was obtained from *E*8 (m.p. 129° to 130° C.) and *S*4 (m.p. 128° to 129° C.).

It behaved as a single substance when subjected to repeated fractional crystallization. In admixture with known substances, it melted as follows:

with 9,10-dihydroxystearic acid of m.p. 132° C., 120° to 123° C.

with 13,14-dihydroxybehenic acid of m.p. 130° C. 123° to 126° C.

with 11,12-dihydroxyeicosanoic acid† of m.p. 130.5° C., 130° to 130.5° C.

Found: C, 70.2, 70.1; H, 11.8, 11.8%; equiv., 347; iodine number, 0.
Calc. for $C_{20}H_{40}O_4$: C, 69.7; H, 11.7%; equiv., 344.5; iodine number, 0.

A portion of the same methyl ester fraction was oxidized by hydrogen peroxide by the method of Hilditch (4). The resulting dihydroxyeicosanoic acid melted at 94° to 95.5° C. It has not been described previously.

In admixture with the corresponding dihydroxy acids prepared from oleic and erucic acids, it melted as follows:

with 9,10-dihydroxystearic acid of m.p. 94° to 95° C., 87° to 89° C.

with 13,14-dihydroxybehenic acid of m.p. 98° to 99° C., 88° to 93° C.

The dihydroxy acid of m.p. 129° to 130° C. was subjected to oxidation by periodate according to the method of Baldwin and Parks (1). The products gave an alkali-soluble semicarbazone, m.p. 156° to 157° C., which depressed the melting point (by more than 10°) of the corresponding semicarbazones prepared in the same way from ordinary oleic and erucic acids. The mixed melting points were as follows:

with azelaic semi-aldehyde semicarbazone of m.p. 162° to 163° C., 140° to 145° C.

with brassylic semi-aldehyde semicarbazone of m.p. 160° to 161° C., 142° to 144° C.

Found: N, 16.2, 16.3%. Calc. for undecanoic semi-aldehyde semicarbazone ($C_{12}H_{23}O_3N_3$) : N, 16.33%.

An alkali-insoluble semicarbazone, m.p. 93° to 94° C., was also isolated. It gave no depression of melting point when mixed with nonaldehyde semicarbazone.

It is concluded from these results that the original acid has nine carbon atoms to the left of the double bond and that the portion of the chain to the right of the double bond has 11 carbon atoms. The original substance is therefore considered to be 11 : 12 eicosenoic acid.

Additional Evidence of the Presence of Eicosenoic Acid

The first indication of the presence of a C_{20} acid was the unexpectedly large fraction (*E*7) of methyl esters distilling midway between the boiling points of the C_{18} and C_{22} esters (see Table III).

There was a similar but smaller intermediate fraction (*S*4) obtained from the *S* esters. The *A* esters did not yield a readily recognizable C_{20} fraction.

The *E* esters therefore appear to contain the largest proportion of C_{20} acid or acids. Eicosenoic acid, if present, would be expected chiefly in the *E* esters, which are prepared from the lead salts of intermediate solubility, i.e., less soluble than lead linoleate but more soluble than lead palmitate. The separation by lead salts is, of course, far from complete.

† *Kindly furnished by Professor Hilditch.*

Fraction *E*7, believed to consist largely of C_{20} acids, had equivalent weight 321 and iodine number 82.6. The corresponding figures for methyl eicosenoate are: equivalent weight, 324; iodine number, 78.2.

The second and positive indication of the presence of eicosenoic acid was obtained by the preparation of dihydroxyeicosanoic acid and comparison with a genuine sample, as described above.

The third indication of a C_{20} acid was the isolation during the permanganate oxidation of a solid, unsaturated acid melting in the neighbourhood of 50° C. This substance was obtained in rather small amounts from the treatment of fractions *E*7, *E*8, *S*4, and *A*7. It was isolated by extracting the resulting mixture of acids with hexane, in which it is soluble. Any saturated acid would, of course, be present with and contaminate it. It was at first thought that it might be the elaidic form of erucic acid, but, on treating genuine erucic acid with alkaline permanganate in the usual way, no such product was found.

The substance can be recrystallized from alcohol. The sample from *E*7 had the following properties: m.p. 47° to 49°C., iodine number, 73; equivalent weight, 319. Eicosenoic acid requires: iodine number, 82; equivalent weight, 310. The low iodine number suggests the presence of saturated acids. An attempt to isolate this acid directly from the *E*7 esters via the lead salt was unsuccessful, the resulting acid having a melting point no higher than 10° to 15° C.

Proportions of Fatty Acids

Calculation of the exact proportions of the various fatty acids requires more data than are available here. Furthermore, the presence of eicosenoic acid, in addition to the common acids, makes the calculation much more difficult. A rough estimate can be made by reference to the distillation data, the quantities of acids isolated from the various fractions, and the iodine numbers of the fractions.

The proportions of certain acids are estimated on this basis as follows (Table VI):

TABLE VI

ESTIMATED PROPORTIONS OF CERTAIN ACIDS (AS METHYL ESTERS)

Acid	*S* acids, gm.	*E* acids, gm.	*A* acids, gm.	Total wt., gm.	Total %
Palmitic	9	2	1	12	2
Other saturated acids	11	0	0	11	2
Linoleic	0	27	45	72	15

The remaining acids are oleic, eicosenoic, and erucic. These three comprise about 80% of the total acids. An estimate of the proportion of each can be made very roughly from the weight of the various fractions obtained in the distillations (Table VII).

TABLE VII

ESTIMATED PROPORTIONS OF ETHYLENIC ACIDS (AS METHYL ESTERS)

Acid	*S* acids, gm.	*E* acids, gm.	*A* acids, gm.	Total wt., gm.	Total %
Oleic	19	91	37	147	29
Eicosenoic	12	31	17	60	12
Erucic	68	89	42	199	40

Calculation of the iodine number from these figures gives a result lower than that for the original oil. Undoubtedly some of the more unsaturated components have been lost by oxidation and polymerization during the process of separation. It may be assumed that the content of linoleic acid is higher than 15%.

The composition of the fatty acids can therefore be given approximately as follows:

Palmitic	2%
Other saturated acids	2
Oleic	20-30
Linoleic	15-20
Erucic	35-45
Eicosenoic	Remainder

The percentage of eicosenoic acid as shown in Table VII is a broad estimate. The author is of the opinion that the amount may be somewhat less than 12% of the total fatty acids.

Discussion

The oil under examination is seen to resemble other Cruciferae oils in having erucic acid as its principal component. The only marked difference from the oils of rape, ravison, and mustard seed is the presence of eicosenoic acid. The author has not found any previous report of positive identification of this acid in vegetable oils. However, it has been isolated from a vegetable wax from the seeds of *Simmondsia californica* (10).

Eicosenoic acid is found in fish and marine animal oils, especially in cod liver oil (3), dogfish liver oil, and sperm oil. There is little information concerning the properties of the isomeric eicosenoic acids on record, and this fact adds to the difficulty of detection and positive identification.

Cis and *trans* 11 : 12 eicosenoic acids were prepared synthetically by Vesely and Chudozilov, who report that the *cis*-form is probably identical with gadoleic acid from cod liver oil, m.p. 23° to 24° C. (12). On the other hand, Toyama has shown by ozonolysis that the cod liver oil acid is 9 : 10 eicosenoic acid (11). Bodenstein prepared 11 : 12 eicosenoic acid by degrading erucic acid and gave the melting point as 50° C. (2). This may be the *trans*-form

which Vesely found to melt at 53° to 54° C. The acid from *Simmondsia* seeds was identified as 11 : 12 eicosenoic acid but its melting point was not stated.

There is no apparent reason for the rarity of eicosenoic acid in the vegetable kingdom. It may occur in small quantity in a number of vegetable oils and have been overlooked by investigators. Examination of the data of Hilditch and co-workers for rapeseed and other Cruciferae oils indicates, however, that if eicosenoic acid is present it must be in comparatively small amount.

It is difficult to account for the fact that rapeseed and ordinary mustard seed oils contain large proportions of oleic (C_{18}) and erucic (C_{22}) acids but apparently no eicosenoic acid (C_{20}). In other fats that have been analysed in detail, all the even-numbered acids are present and form a series without gaps. Two of these are shown in Table VIII.

TABLE VIII

Occurrence of fatty acids in series

Saturated acids in coconut oil (5)		Unsaturated acids in sperm whale blubber (5)		Unsaturated acids in rapeseed oil (5)	
C_8	7.9%	C_{14}	4%	C_{14}	—
C_{10}	7.2	C_{16}	27	C_{16}	—
C_{12}	48.0	C_{18}	37	C_{18}	48%
C_{14}	17.5	C_{20}	19	C_{20}	—
C_{16}	9.0	C_{22}	1	C_{22}	50
C_{18}	2.1				

In the majority of seed fats, C_{16} and C_{18} acids make up almost the whole fatty acid content. The mechanism of elaboration in these seeds must therefore favour the C_{16} and C_{18} chain lengths. Cruciferae seeds have a tendency to secrete C_{22} acid in addition to C_{18} acids. The factor or factors leading to the production of unsaturated C_{20} acids in plants must occur but rarely, although the saturated acid, eicosanoic, is fairly common. In the species described in this paper, there is evidently a tendency to produce minor amounts of eicosenoic acid as well as the C_{18} and C_{22} acids. It may be noted that *Conringia orientalis* differs botanically in many respects from the *Brassica* species. The latter include rape and common mustard, in whose seeds eicosenoic acid has not been found.

Acknowledgment

The author is indebted to Mr. R. G. Davis, who carried out the periodate cleavage of dihydroxyeicosanoic acid and the identification of the cleavage products.

Mr. A. C. Heise, Dominion Department of Agriculture, kindly supplied the weed seeds for this work.

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VAPOUR PHASE OXIDATION OF ETHYL LACTATE[1]

By Marshall Kulka[2]

Abstract

A method has been developed for the vapour phase oxidation of ethyl lactate to ethyl pyruvate (yield, 68%), using air as oxidant and a platinum catalyst prepared by electrolytic deposition.

The oxidation of ethyl lactate in the liquid phase generally results in a low yield of ethyl pyruvate since the latter is susceptible to degradation and further oxidation. Hurd and Filachione (2) were able to prepare ethyl pyruvate in 42% yield by first condensing ethyl lactate with triphenylmethyl chloride and then pyrolyzing the condensate at 300° C. A patent (1) describing a process for the manufacture of esters of oxy-acids claims that ethyl lactate can be oxidized successfully (60% yield) by passing it mixed with air through a pipe 10 metres long, charged with vanadium pentoxide that had been precipitated on pumice stone, and heated at 250° to 255° C.

Mixtures of ethyl lactate and ethyl pyruvate are difficult to separate by fractional distillation because of the proximity of their boiling points (151° to 153° C. and 146° to 148° C. respectively). In this investigation it was decided to search for a catalyst that would direct the oxidation to complete conversion and thus avoid the difficult separation of the oxidation product and starting material. The catalysts that proved unsatisfactory were, copper or brass gauze, copper sulphate reduced with chromous chloride (4), ferrous vanadate (3), copper vanadate (3), vanadium pentoxide on asbestos, and silver on copper gauze with which at temperatures of 250° to 300° C. only a 35 to 50% conversion could be obtained. Platinum gauze coated electrolytically with a layer of platinum black was found to be the most desirable catalyst for this reaction. In the presence of this catalyst oxidation proceeded at a lower temperature and with almost complete conversion (yield, 68%). However, care had to be exercised in the preparation of the platinum surfaces, since platinizing under slightly different conditions produced catalysts varying in degree of activity. The oxidation reaction was extremely exothermic so that the oxidant (air) had to be diluted with inert gases such as nitrogen or steam in order to moderate the reaction.

The life of the catalyst was approximately 45 hr., after which time the activity fell off rapidly. Reactivation could not be accomplished by heating at 400° C. in a stream of air or oxygen nor by treatment with concentrated nitric acid, but heating for one hour at 150° to 175° C. in a solution of 1 part concentrated nitric acid and 10 parts concentrated sulphuric acid regenerated

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.
[2] *Research Chemist.*

the catalyst. This treatment however dissolved a small amount of the platinum surface so that after three or four reactivations most of the platinum black disappeared and a new surface had to be laid by electrolytic deposition.

Experimental

Preparation of the Catalyst

Into a small beaker containing a solution of ammonium chloroplatinate (0.2 gm.) and a trace of lead acetate (about 0.01 gm.) in water (100 cc.) wae introduced a sheet of 52 mesh platinum gauze (diameter 0.004 in.) about 4 by 10 in. weighing 20.35 gm., and a piece of platinum foil about 1 by $1\frac{1}{2}$ in. The foil in cylindrical form placed at the centre of the beaker was connected to a positive terminal of a four-volt battery and the gauze surrounding the foil and about $\frac{1}{2}$ in. away from it was connected to the negative terminal through a variable resistance and an ammeter. The resistance was adjusted so that a current of 0.1 amp. flowed through the circuit. After about 20 min. the current was interrupted, the platinum gauze turned inside out, and the plating continued for another 20 min. In this way a uniform adherent surface of platinum black was obtained. It was washed with water, placed on top of a sheet of somewhat heavier copper gauze equal to its own size, rolled up to make a cylinder 4 in. long, and inserted into the catalyst chamber between two rolls of copper gauze.

Apparatus

The catalyst chamber consisted of an electrically heated vertical glass tube $\frac{3}{4}$ in. in internal diameter and 2 ft. long with a 24 : 40 male ground glass joint at the lower end, a 29:42 female ground joint at the upper end and an outlet tube, about 4 in. below the female joint, connected to a long condenser. This chamber was charged first with a close-fitting roll of copper gauze about 9 in. long, then the prepared catalyst, and finally with a roll of copper gauze 6 in. long. Into the top ground joint was inserted a glass stopper through the middle of which was sealed a thermometer well reaching right into the centre of the platinum catalyst. The temperature of the catalyst could thus be measured by means of a long thermometer or a thermocouple. The bottom ground joint of the catalyst chamber was fitted into one neck of an electrically heated 500 cc. three-necked flask acting as a preheater. Through another neck ethyl lactate was introduced dropwise by means of a siphon containing a grooved stopcock for rate control. The third neck was connected to a Drierite-packed tower, which was connected to a flask receiving air and nitrogen each through separate flowmeters from compressed sources.

Oxidation of Ethyl Lactate

The temperature of the preheater was raised to 200° C. and that of the catalyst to 190° C. by adjusting the resistances of the heaters, and air, nitrogen, and ethyl lactate were introduced into the system at 5 to 5.5 litres per hr., 4.5 litres per hr., and about 4 gm. per hr., respectively. After a few hours of operation the oxidation was initiated, as evidenced by the rise in temperature of the catalyst and by the appearance of two phases (water and ethyl pyru-

vate) in the distillate. During the oxidation, the temperature of the catalyst was maintained at 200° to 230° C. and that of the preheater at 200° C. After 42½ hr. of continuous operation, the catalytic activity began to fall off, as evidenced by a drop in temperature and a decrease in the amount of ethyl pyruvate in the distillate. During this time 154 gm. of ethyl lactate had been fed into the preheater, 149.7 gm. of distillate was collected, and 15.0 gm. (mostly water) was caught in a dry-ice trap. To the distillate was added sodium chloride (1 gm.) in order to aid in the separation of the two layers, and the water layer (26.4 cc.) was removed. To the organic layer an equal volume of chloroform was added and then distilled off together with a small amount of water that was still present in the organic layer. The residual ethyl pyruvate distilled at 144° to 147° C., yielding 103 gm. (68%) of a colourless liquid, $n_D^{20} = 1.4065$, and a small amount of higher-boiling residue. When 0.50 gm. of the distillate was treated with excess semicarbazide hydrochloride and potassium acetate it yielded 0.63 gm. of semicarbazone, melting at 208° to 209° C. The same amount of pure ethyl pyruvate, prepared by esterification of pyruvic acid (5) and purified by fractional distillation, when treated under the same conditions, yielded 0.65 gm. of semicarbazone melting at 208° to 209° C.

Regeneration of the Catalyst

The platinum catalyst was removed from the reaction chamber, separated from the copper gauze, placed into a solution of concentrated nitric acid (10 cc.) and concentrated sulphuric acid (100 cc.), and heated at 150° to 175° C. by means of an oil-bath for one hour. Then it was removed from the acid, washed well with hot water and replaced in the reaction chamber as before. At this stage the life of the catalyst was usually longer than that of the freshly platinized surface.

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CALYCANTHINE

V. ON CALYCANINE[1]

By Léo Marion[2], Richard H. F. Manske,[3] and Marshall Kulka[4]

Abstract

A compound having the structure previously suggested for calycanine has been synthesized. It is a lepidyl-carboline but is not identical with the degradation product from calycanthine. As an alternative structure for calycanine its formulation as a carboline is abandoned and it is suggested that it is a compound formed by fusion of a carbazole and a pyridine nucleus.

Manske and Marion (8) have submitted a tentative structural formula for calycanthine, and, as a consequence of this formula, have suggested a possible structure (I) for calycanine, one of the degradation products of the alkaloid. In the meantime Hargreaves (6) has subjected calycanine to an X-ray investigation and came to the conclusion that the suggested formula of the former authors cannot obtain. Nevertheless the compound of the given formula has been synthesized. It was found to be quite distinct from calycanine. Not only does it melt some 80° C. lower than calycanine, but, in common with most carboline derivatives, it is intensely fluorescent in neutral or acid solutions while calycanine is not or only slightly so. It is therefore unlikely that calycanine is a derivative of carboline.

Superficially no serious obstacle to the synthesis of a substance of formula (I) was to be anticipated. Claisen (2) reported that propargaldehyde condenses with one mole of aniline in the cold and that when the resulting 1-anilino-2-propyn-1-ol is heated with aniline hydrochloride in aqueous solution malondianilide is formed. Analogously an attempt was made to condense propargaldehyde first with *o*-aminoacetophenone and then to condense the resulting 1-(*o*-acetylanilino)-2-propyn-1-ol with tryptamine hydrochloride. The resulting malondianilide derivative on ring closure and elimination of one mole of water should yield a dihydro-derivative of (I). However an attempt to condense 1-(*o*-acetylanilino)-2-propyn-1-ol with tryptamine hydrochloride resulted in a resinous product only. It was then assumed that the condensation of tryptamine with lepidine-3-carboxylic acid would yield the

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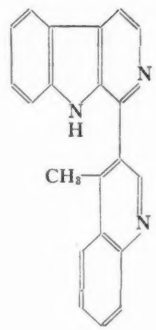
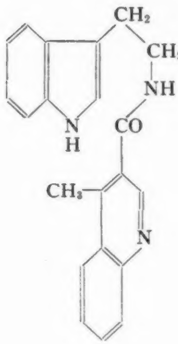
[2] *Chemist, National Research Laboratories.*

[3] *Director of Research, Dominion Rubber Company Limited, Guelph, Ontario.*

[4] *Chemist, Guelph, Ont.*



(I)



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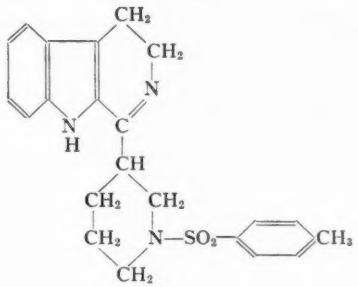


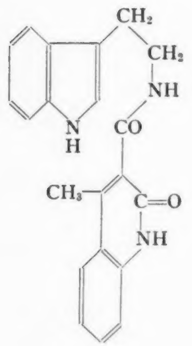
(III)

β-(3-indolylethyl) amide of lepidine-3-carboxylic acid (II) and usual condensing agents used in such cases (phosphorus pentachloride, phosphorus oxychloride, phosphorus pentoxide, etc) would effect ring closure to the dihydro-derivative of (I), which in turn could be readily dehydrogenated to (I). These attempts, however, failed. In a parallel case in which the acid moiety was nicotinic acid, ring closure of the amide again failed. It was then recognized that these amides are still bases and that the condensing agents form addition compounds with them which are unreactive. In a pilot experiment, nicotinic acid was first reduced to its hexahydro-derivative (nipecotic acid) (7), which was converted into its *p*-toluenesulphonyl derivative (4). The acid chloride of the latter was condensed with tryptamine and the resulting amide treated with phosphorus oxychloride in chloroform. Ring closure occurred in the normal manner and the piperidyl-carboline derivative (III) was obtained in good yield.

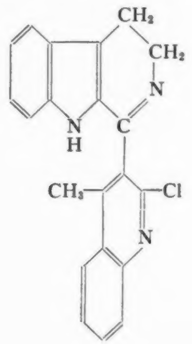
Hydrolysis of (III) occurred when it was heated with 20% hydrochloric acid to yield 3-(3-piperidyl)-5,6-dihydro-4-carboline. The last named compound could not be dehydrogenated successfully by heating with platinum black at 270° C. nor by heating under reflux in tetralin with a little palladium black in a nitrogen atmosphere. In each case low-boiling materials and undistillable neutral resins were formed, indicating degradation.

Attempts to prepare a tetrahydro- or perhydro-lepidine-3-carboxylic acid failed. Reduction occurred but no homogeneous product could be isolated. Attempts to prepare a *p*-toluenesulphonyl derivative of the crude acid likewise failed. Attention was therefore directed to condensing the chloride of 2-lepidone-3-carboxylic acid with tryptamine but the acid could not be converted into its acid chloride.

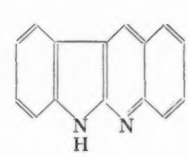
Ultimately a nucleus synthetic procedure was adopted for the preparation of the required amide (IV). An excess of malonic ester was heated with tryptamine to yield the tryptamide of carbethoxyacetic acid. The latter was condensed with *o*-aminoacetophenone, yielding (IV). Ring closure of this



(IV)



(V)



(VI)

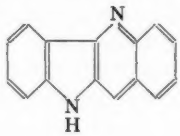
compound with phosphorus oxychloride yielded the chloro-compound (V). The elimination of the chlorine and the removal of two hydrogen atoms from (V) to yield (I) was almost quantitatively achieved by heating the substance with palladium black in tetralin in an atmosphere of nitrogen.

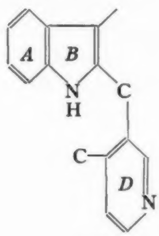
Lepidine-3-carboxylic acid does not appear to have been described. It was obtained from 3-cyano-2-lepidone (1) via the corresponding chloro-compound, namely, 2-chloro-3-cyano-lepidine. The latter was reduced to 3-cyanolepidine with chromous chloride and ultimately hydrolysed to the desired acid.

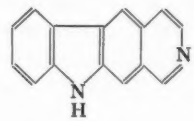
Having disposed of the suggested structure of calycanine, it becomes expedient to re-examine the known evidence in the hope that a rational formula can be proposed. If the assumption is made that the compound is not a carboline derivative, the source of the basic nitrogen must be sought in a pyridine nucleus. The presence of an active hydrogen suggests an indol nucleus but since the Ehrlich colour reaction is negative, it must be substituted in positions 2 and 3. Since molecular weight determinations yield anomalous results, it is impossible to state with certainty its molecular magnitude. The X-ray investigations already referred to point to two nitrogens or a multiple thereof. The choice is therefore almost certainly limited to $C_{15}H_{10}N_2$. The formula $C_{16}H_{10}N_2$ is abandoned. The analytical figures given by Manske and Marion agree better with $C_{15}H_{10}N_2$ than with any other formula containing two nitrogens. (Found: C, 82.57; H, 4.65; N, 12.64%. Calc. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.59; N, 12.85%).

The fusion of an indol nucleus with a benzene and a pyridine nucleus requires $C_{15}H_{10}N_2$, and, since a carboline seems to be excluded, the order of fusion must be that given, that is, the compound might be one formed by the fusion of a carbazole and a pyridine nucleus. No such substances appear to be known at present although quinindoline (VI) (3), which has two of the nuclei interchanged, has solubility and melting point (342° C.) properties similar to caly-

canine. The isomeric quinindoline (VII) (5) melts at 247° C. and its solutions are fluorescent. Angular analogues do not appear to be known.







(VII) (VIII) (IX)

There are 12 possible ways in which a carbazole and a pyridine nucleus may be fused. As a working hypothesis certain assumptions may be made. If it is assumed that pyrolysis of calycanthine eliminates all but rings *A*, *B* and *D* of the proposed structural formula, the skeleton (VIII) may remain. Reorientation and ring closure could lead to (IX), which is considered to be one of the more probable expressions for calycanine.

Experimental

1-(o-Acetylanilino)-2-propyn-1-ol

To 5% sulphuric acid (20 cc.) was added 1.75 gm. propargaldehyde diethyl acetal, the mixture heated to 60° C. and then shaken in a stoppered flask until cool. The heating and shaking were repeated several times until complete solution resulted (about one-half hour). The acid solution was neutralized with solid sodium bicarbonate and then a solution of *o*-aminoacetophenone (1.8 gm.) in ethanol (20 cc.) was added. The yellow needle-like crystals that appeared during the course of one hour (1.8 gm., 70%) were filtered, washed with water and dried, m.p. 128° to 131° C.*; recrystallized from benzene and from ether–ethanol, m.p. 135° to 136° C. Calc. for $C_{11}H_{11}O_2N$: C, 69.84; H, 5.86; N, 7.43%. Found: C, 70.03, 69.74; H, 5.62, 5.76; N, 7.55, 7.53%.

Nicotinic Tryptamide

A solution of nicotinic acid (2.5 gm.), dry pyridine (4 cc.), and thionyl chloride (10 cc.) was heated under reflux for one hour. The excess thionyl chloride was removed under reduced pressure, the residue dissolved in a solution of dry chloroform (15 cc.) and pyridine (4 cc.), and a solution of tryptamine (3.0 gm.) in chloroform (15 cc.) added. The resulting reaction mixture was heated under reflux for one hour, the solvent removed under reduced pressure, and to the dark oily residue 50 cc. of warm 4 *N* hydrochloric acid was added. On cooling, the sparingly soluble hydrochloride of nicotinic tryptamide (3.5 gm.) crystallized as yellow needles, m.p. 141° to 142° C. with decomposition. The hydrochloride was dissolved in a minimum amount of

* *All melting points are corrected.*

hot water and basified with ammonium hydroxide. The oily material that precipitated soon solidified and on recrystallization from benzene containing a little acetone yielded 3.0 gm. (56%) of white microscopic crystals, m.p. 150° to 151° C.; recrystallized from ether containing a little ethanol, m.p. 151° to 152° C. Calc. for $C_{16}H_{15}ON_3$: C, 72.45; H, 5.66; N, 15.85%. Found: C, 72.27, 72.39; H, 5.91, 6.08; N, 15.82, 15.72%.

N-p-Toluenesulphonylhexahydronicotinic Tryptamide

To N-*p*-toluenesulphonylhexahydronicotinic acid (12 gm.) (4) dissolved in dry chloroform (50 cc.) was added thionyl chloride (25 cc.) and the solution heated under reflux for one hour. The solvent and excess reagents were removed under reduced pressure and the light-yellow residue was dissolved in chloroform (100 cc.); pyridine (12 cc.) was added and then a solution of tryptamine (8 gm.) in chloroform (100 cc.). A white precipitate of pyridine hydrochloride appeared immediately. The reaction mixture was refluxed for one-half hour, cooled, washed with dilute hydrochloric acid, with dilute ammonium hydroxide and with water, and the solvent removed. The residual oil which would not crystallize was dissolved in boiling benzene and on cooling yielded white microscopic crystals (10 gm., 56%) m.p. 173° to 174° C., recrystallized from benzene and from ether, m.p. 174° to 175° C. Calc. for $C_{23}H_{27}O_3N_3S$: C, 64.94; H, 6.40; N, 9.88%. Found: C, 65.30, 65.27; H, 6.14, 6.14; N, 9.76, 9.67%.

3-(N-p-Toluenesulphonyl-3-piperidyl)-5,6-dihydro-4-carboline (III)

N-*p*-Toluenesulphonylhexahydronicotinic tryptamide (1.35 gm.) was dissolved in dry chloroform (30 cc.), phosphorus oxychloride (6 cc.) added, and the resulting solution heated under reflux for two hours. The light-yellow precipitate was filtered off, washed with chloroform, dissolved in methanol containing a little concentrated hydrochloric acid, water added, and the solution basified with ammonium hydroxide. The cream-coloured precipitate was filtered off, washed with water and dried, yield, 1.0 gm. (80%), m.p. 236° to 237° C., recrystallized from benzene–petroleum ether, m.p., 236.5° to 237.5° C. Calc. for $C_{23}H_{25}N_3O_2S$: C, 67.78; H, 6.19; N, 10.31%. Found: C, 68.15, 67.79; H, 5.95, 5.90; N, 10.32, 10.54%.

3-(3-Piperidyl)-5,6-dihydro-4-carboline

To 3-(N-*p*-toluenesulphonyl-3-piperidyl-5,6-dihydro-4-carboline (III) (2.0 gm.) was added 20% hydrochloric acid (150 cc.) and the reaction mixture heated under reflux until solution was complete (about 45 hr.). The solution was treated with charcoal, filtered, and the filtrate basified with strong sodium hydroxide solution. The white precipitate was filtered, washed, dried, and recrystallized from acetone, and from methanol, m.p. 195° to 196° C.; yield, 1.0 gm. (80%). It was necessary to heat this compound at 144° C. under a pressure of 1 mm. in order to drive off all the solvent. Calc. for $C_{16}H_{19}N_3$: C, 75.86; H, 7.55; N, 16.60%. Found: C, 75.59, 75.86; H, 7.22, 7.14; N, 16.45, 16.53%.

2-Chloro-3-cyano-4-methylquinoline

3-Cyanolepidone-2 (12 gm.) (1) was added to freshly distilled phosphorus oxychloride (60 cc.) and the reaction mixture heated on the steam-bath for one hour. After it was heated under reflux for seven minutes, most of the excess phosphorus oxychloride was removed under reduced pressure and the residue stirred with water (150 cc.) for a few minutes with cooling. The aqueous suspension was made alkaline with sodium hydroxide and the pink-coloured solid (13 gm.) filtered off, washed with water and air-dried; recrystallization from methanol yielded (11.4 gm., 86%) white needles, m.p. 147° to 148° C. There was no change in melting point when the product was recrystallized from ether. Calc. for $C_{11}H_7N_2Cl$: C, 65.18; H, 3.48; N, 13.82; Cl, 17.53%. Found: C, 64.87, 64.72; H, 3.41, 3.40; N, 13.55, 13.72; Cl, 17.7, 17.8%.

2-Methoxy-3-cyano-4-methylquinoline

2-Chloro-3-cyano-4-methylquinoline (0.3 gm.) was dissolved in methanol (25 cc.), sodium (0.3 gm.) added, and the solution heated under reflux for two hours. The methanol was partially removed, water added, and the white needles (0.2 gm., 68%) filtered, washed, and dried, m.p. 118° to 119° C.; recrystallized from methanol, m.p. 120° to 121° C. Calc. for $C_{12}H_{10}ON_2$: C, 72.73; H, 5.05; N, 14.14%. Found: C, 72.62, 72.71; H, 4.89, 5.14; N, 14.16, 14.18%.

3-Cyano-4-methylquinoline

To a solution of chromic chloride hexahydrate (132 gm.) in concentrated hydrochloric acid (400 cc.) was added amalgamated zinc (140 gm.), and the reduction allowed to continue under an atmosphere of nitrogen until complete, as evidenced by a change in colour from green to blue (several hours). The reaction mixture containing the chromous chloride was decanted into a flask previously swept out with nitrogen and containing 2-chloro-3-cyano-4-methylquinoline (12 gm.). The flask was stoppered and allowed to stand at room temperature for 40 hr. Then it was heated under reflux for one-half hour, cooled, diluted with an equal volume of water, and made alkaline with 30% sodium hydroxide. The precipitate was filtered off, washed, and dried at 45° C. Both the filtrate and precipitate were extracted with boiling benzene, the latter with ten 400 cc. portions. The extracts were combined and the benzene distilled off. The tarry residue was shaken with 10% sulphuric acid (200 cc.) and the insoluble tar filtered off. The acid filtrate was basified and the resulting precipitate (7.7 gm.) filtered, washed, and dried; recrystallization from methanol yielded white needles (5.5 gm., 56%), m.p. 140° to 141° C. This material distilled at about 155° C. (6 mm.), and the distillate, recrystallized from methanol, showed no change in melting point. Calc. for $C_{11}H_8N_2$: C, 78.57; H, 4.76; N, 16.67%. Found: C, 78.61, 78.79; H, 4.94, 4.86; N, 16.53, 16.43%.

3-Carboxy-4-methylquinoline

3-Cyano-4-methylquinoline (7.5 gm.) was added to a solution of sodium hydroxide (10 gm.) in water (40 cc.) and ethanol (80 cc.) and the mixture

heated under reflux until no more ammonia was evolved (six to eight hours). The reaction mixture was taken almost to dryness under reduced pressure, the residue dissolved in water (75 cc.), and the solution treated with 20% sulphuric acid until just slightly acid to congo red. The white solid (7.6 gm., 90%) was filtered, washed, and dried, m.p. 224° to 229° C. with decomposition; recrystallized from water containing a little acetic acid and from methanol, m.p. 232° to 233° C. with decomposition (rate of heating 4° C. per min). Calc. for $C_{11}H_9NO_2$: C, 70.59; H, 4.81; N, 7.49%. Found: C, 70.78, 70.96; H, 4.93, 4.86; N, 7.27, 7.33%.

Tryptamide of 3-Carboxylepidone-2 (IV)

A solution of tryptamine (5 gm.) and ethyl malonate (20 gm.) was heated under gentle reflux (temperature remained at 150° to 160° C. and finally rose to 195° C.) for 30 min. in a flask fitted with a steam-heated condenser. The excess ethyl malonate was removed under reduced pressure and to the residual oily crude malonic ester amide *o*-aminoacetophenone (4.5 gm.) was added. The resulting solution was heated to 190° to 200° C. and kept at that temperature for one-half hour, the volatile products of the reaction (ethanol and water) being allowed to distil off through a steam-heated condenser. The reaction mixture, which solidified to a hard cake, was pulverized and washed well with cold methanol, yielding 4.8 gm. (40%) of white solid, m.p. 280° to 286° C. insoluble in dilute acids, sodium hydroxide, benzene, acetone, and ethyl acetate, and soluble in glacial acetic acid; recrystallized from butanol, m.p. 285° to 287° C. Calc. for $C_{21}H_{19}O_2N_3$: C, 73.03; H, 5.55; N, 12.17%. Found: C, 73.09, 73.35; H, 5.16, 5.36; N, 11.92, 11.61%.

3-(2-Chloro-3-lepidyl)-5,6-dihydro-4-carboline (V)

To the tryptamide of 3-carboxylepidone-2 (IV) (3.5 gm.) was added phosphorus oxychloride (50 cc.) and the mixture heated on the steam-bath for one and a quarter hours. The excess phosphorus oxychloride was distilled off under reduced pressure and to the residue dilute ammonium hydroxide was added. The yellow insoluble solid was filtered, washed with water, dissolved in a solution of ethanol (50 cc.), water (25 cc.), and concentrated hydrochloric acid (10 cc.) and added to water (150 cc.). The solution was treated with charcoal, filtered, the filtrate basified with ammonium hydroxide, and the cream-coloured precipitate (3.0 gm., 85%) filtered, washed, and dried. Recrystallization from benzene and from ethyl acetate yielded white needles, m.p. 215° to 216° C. Calc. for $C_{21}H_{16}N_3Cl$: C, 72.92; H, 4.66; N, 12.15; Cl, 10.28%. Found: C, 72.77, 72.83; H, 4.56, 4.64; N, 12.04, 12.16; Cl, 10.20, 10.60%.

3-(3-Lepidyl)-4-carboline (I)

A mixture of 3-(2-chloro-3-lepidyl)-5,6-dihydro-4-carboline (V) (1.8 gm.), tetralin (100 cc.) and palladium dust (0.3 gm.) was heated under reflux for 20 hr. and the hydrogen chloride liberated was determined by sweeping out with nitrogen into a solution of silver nitrate. In six hours 80% of the hydrogen chloride was liberated and in 20 hr. 93%. The tetralin solution

was decanted from the palladium, extracted with dilute hydrochloric acid, and back-extracted with ether. The acid solution was warmed and basified with sodium hydroxide. The cream-coloured precipitate was filtered, washed with water, dried, and distilled; b.p. about 240° C. (1 mm.). The glassy-like distillate (1.2 gm.) was dissolved in benzene, and, on standing overnight, the solution deposited microscopic yellow crystals losing solvent of crystallization at 185° C. (1.0 gm., 63%), m.p. 230° to 231° C. after drying at 114° C. and 1 mm. for several hours. Recrystallization from dilute ethanol yielded white plates sintering at 150° C. after drying at 110° C. and 15 mm. pressure; and melting at 231° to 232° C. after drying at 144° C. and 1 mm. pressure. Calc. for $C_{21}H_{15}N_3$: C, 81.55; H, 4.86; N, 13.58%. Found: C, 81.80, 81.68; H, 4.56, 4.42; N, 13.63, 13.58.

This compound when heated with platinum in an atmosphere of nitrogen at 250° C. for several hours liberated no hydrogen and remained unchanged.

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PARACHOR OF CERTAIN AZOXY AND RELATED AZO COMPOUNDS[1]

By H. E. Bigelow[2] and K. F. Keirstead[3]

Abstract

The parachors of certain azoxy and related azo compounds have been found. Values for the N_2O group have been calculated from the constants of Sugden and from the recalculated values of Mumford and Phillips. In most cases the experimentally determined values agree better with the values calculated from Sugden's data. Possible explanations for anomalous parachors are discussed.

Introduction

Although the parachors of many organic compounds have already been determined (8), relatively few values have been obtained for the azoxy compounds and their derivatives. The parachors of azoxybenzene (7), azoxytoluene (1), *p*-azoxyanisole (5), *p*-azoxyphenetole (5), ethyl azoxyisopropyl ketone (1), azoxyisopropyl isobutyl ketone, 2-azoxy-2-5-dimethylhexane (1), and ethyl 2-methyl-2-azoxypropionate (1) have been determined. Good agreement was found between experimental values and values calculated on the basis of the open structure of N_2O. The purpose of this investigation is to determine the value of the parachors for various azoxy derivatives and related compounds that have been prepared in these laboratories.

From the examination of the data for isomeric substance and of members of homologous series, S. Sugden (1924) showed (7) the parachor to be primarily an additive, and also a constitutive, property. In view of the appreciable contribution made by structural factors, it is evident that the parachor may be used to decide between alternate configurations provided there is an appreciable difference in structural factors. It may be expected that study of the parachors of azoxy compounds would throw some light on the structural problems of these compounds.

Parachor values have been calculated by us from the constants given by Sugden (8) and from our own measurements. In addition, parachor values have been calculated from the recalculated values and "strain constants" given by Mumford and Phillips (4). In most cases the experimentally determined values agree better with the values calculated from Sugden's data.

From the study of the parachors of azoxybenzene, the value for the group N_2O is calculated by Sugden, Reed, and Wilkins (9) to be 66.7. The mean value from the compounds studied here is 59.2.

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Contribution from the Department of Chemistry, Mount Allison University, Sackville, N.B.

[2] *Carnegie Professor of Chemistry.*

[3] *Present address: New Quebec High School, Quebec, Que.*

TABLE I

VALUE OF N_2O GROUP

	From Sugden's constants	From constants given by Mumford and Phillips
1. *m-m'*-Dibromoazoxybenzene	54.2	48.8
2. *m-m'*-Dichloroazoxybenzene	57.9	53.1
3. *o-o'*-Dichloroazoxybenzene	49.3	44.5
4. *p-p'*-Dichloroazoxybenzene	53.9	49.1
5. *o*-Nitro-*p-p'*-dichloroazoxybenzene	72.3	66.4
6. Trinitro-*m-m'*-dichloroazoxybenzene	70.0	52.5
7. *m-m'*-Dichlor-*o-o'*-dichloroazoxybenzene	59.1	49.5
8. *p*-Nitro-*m-m'*-dichloroazoxybenzene	57.5	51.6
Mean	59.2	51.9

Experimental Part

Densities were determined with a calibrated pycnometer as used by Sugden (8, p. 203), suspended in a bath at a temperature a few degrees above the melting point of the compound. Surface tensions were measured by the method of maximum bubble pressure as described by Sugden (6, 8).

The surface tension (2) is found by this formula:—

$$= A.P.\left(1 + 0.69 \, . \, r_2 \, . \, \frac{gD}{P}\right),$$

where A is an empirical constant characteristic of the apparatus, P is the difference in pressure (dynes) per square centimetre required to liberate bubbles from the two capillaries, g is the acceleration of gravity, D is the density (grams per cubic centimetre) of the melted compound, and r_2 is the radius (in centimetres) of the larger capillary.

The parachor is found by Macleod's equation

$$P = \frac{M\gamma^{\frac{1}{4}}}{D - d},$$

where M is the molecular weight of the compound, γ is the surface tension as determined above, D is the density of the melted compound as above, and d is the density of the vapour. In all determinations the temperature was kept within a few degrees of the melting point. In such cases the value of d is small and is neglected as in Sugden's determination of the parachor of solid compounds (7).

Whenever possible several determinations were made of both the density and the surface tension. In some cases one determination only could be made on account of the limited supply of the sample or on account of the rapid darkening of the bath at high temperatures. Fisher Bathwax showed little darkening below 150° C. At higher temperatures the bath darkened rapidly, finally making it impossible to read the pycnometer.

(1) *m-m'*-Dibromoazoxybenzene,

$C_{12}H_8Br_2N_2O$, M = 356, m.p. = 111° C.

$D_{4°}^{120°} = 1.672$	$\gamma^{120°} = 39.92$	whence [*P*]	−536
$D_{4°}^{117°} = 1.668$	$\gamma^{117°} = 41.44$	whence [*P*]	−536
		mean [*P*]	−536
		[*P*] calc.	−548.4(S)
			−554.7 (M&P)

(2) *m-m'*-Dichloroazoxybenzene,

$C_{12}H_8Cl_2N_2O$, M = 267.2, m.p. = 97° C.

$D_{4°}^{105°} = 1.296$	$\gamma^{105°} = 38.07$	whence [*P*]	−512.3
		[*P*] calc.	−521.0(S)
			−526.7(M&P)

(3) *o-o'*-Dichloroazoxybenzene,

$C_{12}H_8Cl_2N_2O$, M = 267.2, m.p. = 56° C.

$D_{4°}^{63°} = 1.325$	$\gamma^{63°} = 38.95$	whence [*P*]	−503.7
		[*P*] calc.	−521.0(S)
			−526.7(M&P)

(4) *p-p'*-Dichloroazoxybenzene,

$C_{12}H_8Cl_2N_2O$, M = 267.2, m.p. = 152.7°C.

$D_{4°}^{159°} = 1.250$	$\gamma^{159°} = 33.62$	whence [*P*]	−514.6
$D_{4°}^{157°} = 1.270$	$\gamma^{157°} = 33.60$	whence [*P*]	−507.2
$D_{4°}^{161°} = 1.265$	$\gamma^{161°} = 32.50$	whence [*P*]	−503.6
		mean	−508.3
		[*P*] calc.	−521.0(S)
			−526.7(M&P)

(5) *o*-Nitro-*p-p'*-dichloroazoxybenzene,

$C_{12}H_7Cl_2N_3O_3$, M = 311.9, m.p. = 137° C.

$D_{4°}^{140°} = 1.329$	$\gamma^{140°} = 39.53$	whence [*P*]	−588.0
$D_{4°}^{140°} = 1.340$	$\gamma^{140°} = 38.02$	whence [*P*]	−578.3
$D_{4°}^{143°} = 1.322$	$\gamma^{143°} = 37.69$	whence [*P*]	−584.7
		mean	−583.7
		[*P*] calc.	−578(S)
			−584.8(M&P)

(6) Trinitro-*m-m'*-dichloroazoxybenzene,

$C_{12}H_5Cl_2N_5O_7$, M = 402, m.p. = 182° C.

$D_{4°}^{188°} = 1.429$	$\gamma^{188°} = 37.25$	whence [*P*]	−695.0
		[*P*] calc.	−692(S)
			−701.0(M&P)

(7) *m-m'*-Dichloro-*o-o'*-dichloroazoxybenzene,

$C_{12}H_6Cl_4N_2O$, M = 335.9, m.p. = 147° C.

$D_{4°}^{150°} = 1.392$	$\gamma^{150°} = 35.24$	whence [*P*]	−587.9
		[*P*] calc.	−595.4(*S*)
			−605.9(M&P)

(8) *o*-Nitro-*m*-*m*′-dichloroazoxybenzene,

$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. $= 112°$ C.

$D_{4^\circ}^{117^\circ} = 1.382$	$\gamma^{117^\circ} = 36.00$	whence [*P*]	−553.0
$D_{4^\circ}^{120^\circ} = 1.377$	$\gamma^{120^\circ} = 36.29$	whence [*P*]	−556.1
$D_{4^\circ}^{124^\circ} = 1.375$	$\gamma^{124^\circ} = 36.29$	whence [*P*]	−557.0
		mean	−555.3
		[*P*] calc.	−578.0(S)
			−587.8(M&P)

(9) *p*-Nitro-*m*-*m*′-dichloroazoxybenzene,

$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. $= 145°$ C.

$D_{4^\circ}^{151^\circ} = 1.374$	$\gamma^{151^\circ} = 39.70$	whence [*P*]	−569.8
$D_{4^\circ}^{148^\circ} = 1.377$	$\gamma^{148^\circ} = 39.06$	whence [*P*]	−568.0
		mean	−568.9
		[*P*] calc.	−578.0(S)
			−584.8(M&P)

(10) *m*-Nitro-*p*-nitro-*m*-*m*′-dichloroazoxybenzene,

$C_{12}H_6Cl_2N_4O_5$, $M = 367$, m.p. $= 157°$ C.

$D_{4^\circ}^{165^\circ} = 1.482$	$\gamma^{165^\circ} = 41.03$	whence [*P*]	−671.9
$D_{4^\circ}^{164^\circ} = 1.488$	$\gamma^{164^\circ} = 42.32$	whence [*P*]	−674.1
$D_{4^\circ}^{160^\circ} = 1.493$	$\gamma^{160^\circ} = 41.62$	whence [*P*]	−668.6
		mean	−671.5
		[*P*] calc.	−635.0(S)
			−642.9(M&P)

(11) Trinitro-*m*-dichloroazoxybenzene,

$C_{12}H_5Cl_2N_5O_7$, $M = 402$, m.p. $= 165°$ C.

$D_{4^\circ}^{170^\circ} = 1.482$	$\gamma^{170^\circ} = 38.95$	whence [*P*]	−677.7
$D_{4^\circ}^{172^\circ} = 1.482$	$\gamma^{172^\circ} = 37.24$	whence [*P*]	−670.2
$D_{4^\circ}^{173^\circ} = 1.505$	$\gamma^{173^\circ} = 39.74$	whence [*P*]	−670.8
		mean	−672.9
		[*P*] calc.	692(S)
			701.0(M&P)

(12) Hydroxy-*o*-*o*′-dichloro-*m*-*m*′-dichloroazobenzene,

$C_{12}H_6Cl_4N_2O$, $M = 335.9$, m.p. $= 128°$ C.

$D_{4^\circ}^{135^\circ} = 1.455$	$\gamma^{135^\circ} = 39.23$	whence [*P*]	−578.1
		[*P*] calc.	−587.0(S)
			−600.5(M&P)

(13) *p*-Hydroxyazobenzene,

$C_{12}H_{10}N_2O$, $M = 198.2$, m.p. $= 152°$ C.

$D_{4^\circ}^{160^\circ} = 1.089$	$\gamma^{160^\circ} = 37.35$	whence [*P*]	−466.2
$D_{4^\circ}^{157^\circ} = 1.092$	$\gamma^{157^\circ} = 36.60$	whence [*P*]	−446.3
		mean	−446.4
		[*P*] calc.	−448.2(S)
			−442.1(M&P)

(14) 2,4-Benzene-bis-azophenol,

$C_{18}H_{14}N_4O$, $M = 302.1$, m.p. $= 131°$ C.

$D_{4°}^{137°} = 1.122$ $\gamma^{137°} = 37.16$ whence $[P]$ -664.9

$[P]$ calc. -626.1(S)

-664.2(M&P)

(15) A Trinitro-*p*-*p'*-dichloroazoxybenzene,

$C_{12}H_5Cl_2N_5O_7$, $M = 402$, m.p. $= 189°$ C.

This compound being melted in a bath at 193° C., rapid decomposition set in, ending in a puff of dense black smoke. This compound was prepared by Bigelow and Wasson.

(16) *o*-Nitro-*m*-*m'*-dichloroazoxybenzene,

$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. $= 116°$ C.

$D_{4°}^{120°} = 1.666$ $\gamma^{120°} = 45.52$ whence $[P]$ -482.3

$D_{4°}^{121°} = 1.635$ $\gamma^{121°} = 39.61$ whence $[P]$ -478.8

mean -480.5

$[P]$ calc. -578.0(S)

-584.8(M&P)

Discussion

The compounds used in this study were all prepared in these laboratories and the melting point taken with stem correction. In cases of new compounds, they were purified to constant melting point. The structures of compounds (6), (8), (9), (10), (11), (12), (15), and (16) have not been fully established. In some cases the evidence for the position of one or more substitutes is lacking and hence the position of such groups is not indicated in the name. Compounds (6), (8), (9), (10), (11), and (16) were prepared and described by Bigelow and Steeves (2).

The parachor values calculated from the constants given by Sugden (8) and from our own measurements are in good agreement except for compounds (8), (10), (11), and (16). Since the structures of these compounds have not been fully determined, we must consider the possibility that some alternate structure, such as a cyclic structure, would better correspond to the properties of the compound and to its parachor.

Compound (8) is believed to have the nitro group in the ortho position, but unlike similar compounds, it could not be reduced to the corresponding amine.

The anomalous parachor value for compound (10) was probably due to partial decomposition. No unusual signs of decomposition were seen while the compound was melted. However, chromatographic analysis of the material after melting and cooling showed that some decomposition took place during the heating. When Fisher Adsorption Alumina was used as the adsorbent and a mixture of benzene and ethanol as the solvent, the developed chromatogram showed the presence of two dyes: a bright red dye in the upper portion and a yellow one in the lower portion. No adsorption was evident in

the case of the compound before melting. The red dye was soluble in water, and was of a straw colour in acid solution; melting point of red dye, 75° to 80° C.; melting point of hydrochloride of red dye, 132° to 135° C.

Chromatographic analysis was also used to study compound (11) after melting. The developed chromatogram showed the presence of red dyes, thus giving evidence for some thermal decomposition. Not enough of the dye was present to permit comparison of its properties with the red dye produced from compound (10).

Compound (16), whose experimentally determined parachor showed the greatest deviation from the calculated value, showed no signs of decomposition when the material after heating was subjected to chromatographic analysis. Instead of being an azoxy compound as originally described by Bigelow and Steeves (2), compound (16) is more likely *p'*-hydroxy-*o*-nitro-*m*-*m'*-dichloroazobenzene. This compound is highly soluble in water to give a yellow solution suggesting an azo compound. It is also soluble in basic solution, indicating the presence of a hydroxy group. However, the azo form alone would not account for the low parachor since this form would have a parachor greater by the value of the semipolar double bond (1.6).

In the opinion of the authors no reliable conclusions can be drawn from the limited data presented in this paper. It is hoped that a further study can be made of a greater variety of azoxy compounds. As shown in this paper, the experimentally determined parachor value may throw doubt upon the structure assigned to a compound as in the case of compound (8).

Two of the compounds showing anomalous parachors, compounds (8) and (16), have a nitro group in the ortho position and a chloro group in the meta position.

Similar peculiarities of ortho substituted compounds are found in the literature. Gibling (3) reports that the parachors of *o*-hydroxy-derivatives of benzaldehyde, methyl benzoate, and *p*-methoxybenzaldehyde are 2 or 3% less than the calculated values, while those of the *m*- and *p*-compounds are more nearly normal. A further study of such compounds may disclose a diminution of molecular volume brought about either by a closer packing of groups within the molecule, or by a decrease in the effective size of one or other of the atoms concerned, as suggested by Mumford and Phillips (4).

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LX. STABILIZING ACTION OF ETHANOL ON STARCH NITRATES[1]

By W. R. Ashford[2], L. M. Cooke[3], and Harold Hibbert[4]

Abstract

Fractional dissolution has been applied to nitrated corn starch with the consequent removal of ethanol-soluble fractions. Hot and cold ethanol-soluble fractions have been removed in this way amounting to from 10 to 25% of the crude nitrate. The ethanol-soluble fractions, consisting of low-molecular weight and low nitrogen-content material, are not stabilized by ethanol The insoluble portion is greatly stabilized as a result of the ethanol treatment.

The insoluble residue left after ethanol treatment of crude starch nitrate possesses good explosive properties, a high nitrogen content, and high stability. The stabilization of starch nitrate by ethanol is shown to be the result of a dual action, namely, (*a*) removal of highly unstable material of low molecular weight and nitrogen content, and (*b*) the conferring of increased stability by some, as yet unknown, mechanism on the insoluble portion.

Discussion

While the stabilizing action of ethanol upon starch nitrate has been described before (7) its mode of action has not been investigated. Methanol also has been described as a stabilizing agent by Berl and Kunze (2). Ethanol treatment of whole starch nitrate was investigated firstly in an attempt to produce a stable product by this means and secondly to discover something about its mode of action.

Starch nitrate, prepared by nitrating dry corn starch with fuming nitric acid according to the method of Will and Lenze (9), was used in these experiments. The nitrate, after receiving stabilizing boils in water, was subjected to extraction with cold ethanol (95%) which resulted in the removal of 8 to 10% of the crude nitrate as soluble material. In some cases further treatments with hot ethanol, acetone–ethanol, and ether (Fig. 1) were applied, resulting in the extraction of 20 to 25% of the nitrate.

In order that solution of a solid substance may occur, solvation forces must overcome the two cohesions (van der Waal's forces) existing between molecules of solute and of solvent respectively. The solute cohesion in the case of a polymer is determined by the shape and length of the chain, and is usually

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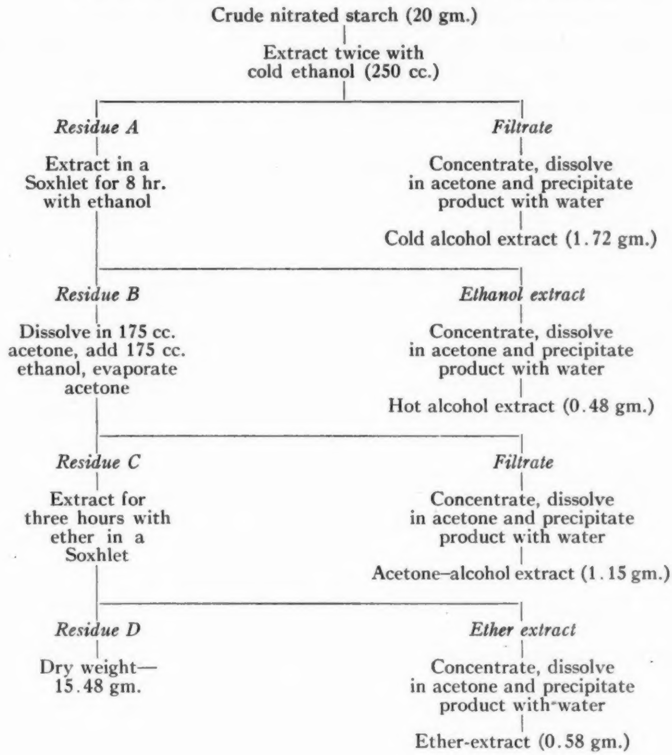
[2] *Holder of a Fellowship under the National Research Council of Canada, 1942-43. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[3] *Sessional Lecturer, 1941-42, Division of Industrial and Cellulose Chemistry, McGill University. Present address: Corn Products Refining Co., Argo, Ill.*

[4] *Late Professor of Chemistry, Division of Industrial and Cellulose Chemistry, McGill University.*

FIG. 1. FRACTIONAL DISSOLUTION OF WHOLE STARCH NITRATE



much smaller for branched chain polymers than for the linear chain type; the latter are therefore much more soluble. The extent of solvation is also determined by the chemical nature of the groups attached to the polymer chain, especially in relation to the chemical structure of the solvent.

The fractional dissolution method was fully developed and tested first with cellulose nitrate (11.4% N) by Rogowin and Glasman (8) who claim important advantages for the method over the technique employing fractional precipitation. One disadvantage of the dissolution method, however, is that solute and solvent are not in complete and intimate contact, i.e., the process involves a heterogeneous system.

The solubility of a nitrated starch depends upon (i) its chain length, (ii) its degree of association and the power of the solvent to break hydrogen bonds, and (iii) the nitrogen content. At the end of the nitration reaction, there is present a heterogeneous mass of varying chain lengths, degrees of association, and nitrogen contents. Thus the use of fractional dissolution for the fractionation of starch nitrate permits a separation based on both physical and chemical

properties. Shorter, non-associated chains, especially those of lower nitrogen content, are removed, leaving a product that may be visualized as a micellar mass formed of tightly interlocking chains. The amount of this residual product will depend upon the dissociating power of the solvent used. With 95% ethanol, the residue constitutes about 90% of the crude nitrate (Residue *A*, Fig. 1).

The characteristics of the ethanol-insoluble fraction and ethanol-soluble fraction are given in Table I. Here the results of the fractionation of two different nitrates are given. The nitrate described in experiment No. 1 resulted from a nitration period of seven hours while the nitrate described under experiment No. 2 was produced by nitrating for a period of 24 hr. The effect of this longer nitration period is readily noticeable in the specific viscosities of the two nitrates. Apparently the longer nitration period caused considerably more degradation of the starch molecules. The nitrogen content of the readily extractable fractions was, in all cases, lower than that of the residual products, being about 8 to 9% in the various ethanolic fractions investigated. Viscosity determinations on the ethanol-soluble fractions (Table I) showed considerable variation in molecular complexity. The lower specific viscosity is not surprising since shorter chains show greater solubility in ethanol and in solvents generally.

TABLE I

CHARACTERISTICS OF PRODUCTS OBTAINED FROM WHOLE STARCH NITRATE BY FRACTIONAL DISSOLUTION

Fraction	N content, %*	η_{sp}, specific viscosity†	Abel value, min.
Expt. No. 1 . . . . Starch nitrated for 7 hr.			
Cold ethanol extract	9.1	0.1910	—
Hot ethanol extract	8.81	0.5777	—
Acetone–ethanol extract	10.55	0.8129	—
Residual product (*D*, Fig. 1)	13.43	—	55
Residual product: (*D*, Fig. 1)	Ignition point—183° C. Brown fumes —165° C.		
Expt. No. 2 . . . . Starch nitrated for 24 hr.			
Cold ethanol extract	8.89	0.0357	—
Acetone–ethanol extract	10.63	0.4050	—
Residual product	13.96	0.509	30
Residual product:	Ignition point—185° C. Brown fumes —173° C.		

* *N content determined by ferrous sulphate method (3) checked by Dupont nitrometer (4, pp. 401-423).*

† *Specific viscosity determined by capillary flow method (5) in acetone at 25° C.*

The ethanol-soluble portion of all starch nitrates examined was found to have a lower stability than the residual product as judged by the Abel test (Table II).

TABLE II

STABILITIES OF PRODUCTS FROM FRACTIONAL DISSOLUTION OF STARCH NITRATE

Fraction	Abel stability, min.
Unfractionated nitrate	3
1. Cold ethanol extract	3
2. Hot ethanol extract	7
3. Acetone–ethanol extract	25
4. Ether extract	20
5. Residual product (*D*, Fig. 1)	40

The residual product (*D*, Fig. 1) from different nitrates examined had Bergmann–Junk values ranging from 2.27 to 2.97 mgm. of nitrogen evolved, while samples of unfractionated nitrate were so unstable under the conditions of this test that in some instances the test could not be applied. Thus, in the case of whole starch nitrate, ethanolic extraction with consequent removal of low-molecular weight material results in an appreciable increase in stability. The maximum instability allowed commercially in the case of cellulose nitrate is that corresponding to an evolution of 1.25 mgm. of nitrogen per gram of sample.

The residual product (*D*, Fig. 1) from the ethanol treatment of starch nitrate, which proved to be of good stability by means of the Abel and Bergmann–Junk tests, was subjected to (*a*) the ignition, (*b*) the machine impact, and (*c*) the Trauzl lead block tests (Table III).

In the ignition test, brown fumes appeared at a lower temperature (about 170° C.) than in the case of cellulose nitrate (182° C.). Also, the actual ignition temperature was about 5 degrees lower. The machine impact test indicated a sensitivity some two to three times greater than that of trinitrotoluene. The Trauzl lead block test showed a net expansion of 358 cc. as compared with trinitrotoluene, 254 cc.; nitroglycerine, 540 cc.; tetranitromethylaniline, 375 cc.; dynamite, 300 cc.; and cellulose nitrate, 290 cc. (1, pp. 179-181).

From the above results, it is evident that starch nitrate contains unstable components of low molecular weight and nitrogen content which are readily extractable by cold ethanol. These components (Table II) are not stabilizable by treatment with ethanol as is the main body of the nitrate (Table III). Thus ethanol presumably functions in a dual capacity, namely, as an extractant for certain unstable portions of starch nitrate and as a stabilizer for the higher molecular-weight material.

TABLE III

EXPLOSIVE CHARACTERISTICS OF ETHANOL-INSOLUBLE STARCH NITRATE

Moisture, %	Ignition temperature		Machine impact test		Sensitivity times T.N.T. T.N.T. = 1	%N*	Abel test, min.
	Ignites, ° C.	Brown fumes, ° C.	Hammer drop, cm.	Hammer drop, % T.N.T. = 100%			
	Residual product, Expt. 1, Table I.						
0.68	183 with flame	167	44	27.5	3.64	13.43	55
	Residual product, Expt. 2, Table I.						
0.55	185 with flame	173	58	36.2	2.76	13.96	30
Trauzl lead block test (50% of each product). Net expansion—358 cc. Net expansion, T.N.T. Standard—256 cc.							

* *N content by Dupont nitrometer (4, pp. 401-423).*

Experimental

Nitration

The nitration procedure of Will and Lenze (9) was followed with modifications. A typical nitration procedure is as follows. Concentrated nitric acid (sp. gr. 1.5, 1200 cc.) in a three litre, three-necked flask, fitted with a stirring motor, was placed in a brine bath at a temperature of $-7°$ C. Unmodified corn starch (120 gm.) was added to the mixture over a period of 45 min., during which time the mixture was stirred vigorously, and the temperature maintained at $-7°$ C. Nitration was completed by continuing the stirring in nitric acid for a period of six hours at the same temperature and then adding concentrated sulphuric acid (600 cc.) over a period of one and one-half hours. The nitrated starch was isolated by pouring the nitration mixture on to vigorously stirred, finely chopped ice and the product separated by filtration. It was washed on the filter with large quantities of cold distilled water, placed in a three-necked flask fitted with a reflux condenser, and boiled for at least 150 hr. using two changes of water, one after 50 and the second after 100 hr., respectively. At the end of this period, the product was filtered and an aliquot portion cautiously dried and weighed. Yield, 204 gm. or 170%*.

Fractional Dissolution of Whole Starch Nitrate

Ethanol (95 to 98%) was used as the solvent in these fractional dissolution studies. The nitrated starch was dried (at 55° C.), prior to treatment, as the presence of more than 5% water greatly reduces the solubility of nitrated starch in ethanol. Ethanolic extraction was carried out by suspending the

* *% yields are based upon the theoretical value for starch nitrate (182.7 gm. from 100 gm. starch).*

starch nitrate (20 gm.) in ethanol (250 cc.) and stirring the mixture vigorously at room temperature for three hours, the process being twice repeated. In most cases, it was necessary to grind the nitrate in ethanol in a mortar in order to remove lumps. The undissolved residue was separated by filtration.

The ethanolic extract was concentrated to small volume (50° C., 20 to 25 mm.) until the dissolved nitrate precipitated. Precipitation was completed by the addition of petroleum ether. The nitrate was separated by filtration and petroleum ether removed by drying at 50° C. The product was then boiled with water (2 litres) under reflux for 15 to 20 hr. to ensure removal of the ethanol. The insoluble residue was treated in a similar manner. About 8 to 10% of the total nitrate was removed in this way.

The extraction of starch nitrates with ethanol was extended in certain cases to include further extractions as recommended by Will and Lenze (9). The procedure was as follows (Fig. 1). Nitrated starch (20 gm.) was extracted by stirring at room temperature with two portions of ethanol (250 cc., 98%) for periods of three hours. The undissolved residue was removed by centrifuging and then extracted for a period of eight hours in a Soxhlet, using ethanol as the solvent. The residue left after this treatment was dissolved in acetone and an equal volume of ethanol (98%) added to the mixture. When the acetone was removed under reduced pressure, the nitrated starch precipitated from the remaining ethanol. The solution and residue were separated by centrifugation. The dried product remaining from the acetone–ethanol treatment was then extracted for three hours with diethyl ether in a Soxhlet. The residue was placed in three litres of distilled water and boiled at reflux temperature for 20 hr. to remove traces of solvent. A small aliquot portion was dried (55° C.) and the remainder left in the wet condition until needed.

The various ethanolic extracts obtained by cold ethanol extraction, hot ethanol extraction, and by acetone–ethanol treatment were each concentrated at 50° C. (20 to 25 mm.) to small volume. Each precipitated nitrate was dissolved in a small quantity of acetone and precipitated by the addition of water. The products were washed by boiling with water at reflux temperature.

Determination of Nitrogen Content

Nitrogen contents were obtained using a modified Bowman–Scott method (3) and the Dupont nitrometer method (4, pp. 401-423). The Bowman–Scott method was carried out as follows.

(*a*) *Preparation of Reagents*

Standard nitric acid was prepared of such strength that 1 cc. of the solution contained approximately the same quantity of nitrogen as a sample of starch nitrate weighing 0.05 gm. and containing 12.5 to 13.0% nitrogen. Standard ferrous sulphate ($FeSO_4 . 7H_2O$) solution was prepared of such strength that about 5.0 cc. of the solution was equivalent to 1 cc. of the above standard nitric acid solution when used according to the conditions of the Bowman–Scott method. The nitric acid and ferrous sulphate solutions

usually employed were 0.45 N and 0.25 M respectively. The strength of the ferrous sulphate solution was determined in terms of grams of nitrogen per cubic centimetre, before each set of analyses by titration against a standard nitric acid solution in the following manner. A 1 cc. sample of standard nitric acid was added slowly and with cooling to concentrated sulphuric acid (25 cc.). The samples were then placed in an ice-bath, and in turn titrated to a permanent end-point (colourless to pinkish-brown) with standard ferrous sulphate solution. The equivalence of 1 cc. of ferrous sulphate solution in grams of nitrogen is given by the expression

$$\frac{1}{1000} \times \frac{\text{Normality } HNO_3 \times 14}{\text{cc. } FeSO_4 \text{ used.}}$$

(*b*) *Determination of Nitrogen*

The samples were dried at 63° C. for a period of three hours in an Abderhalden apparatus. Duplicate samples of about 0.05 gm. were weighed out and dissolved in 25 cc. of concentrated sulphuric acid at room temperature. The samples were then titrated as described above.

Determination of Stabilities

(*a*) *The Abel Heat Test*

All essential features of the standard Abel test were included in the procedure followed (6, pp. 644-660). The important modification was the introduction of thermostatic control to maintain a temperature of 76.7° C. (170° F.). The bath used consisted of a metal container about 12 in. deep and 10 in. in diameter with a tightly fitting, removable lid. The outside surface of this vessel was surrounded by several layers of asbestos. Through separate orifices in the lid there were fitted a strong mechanical stirrer, a thermoregulator and a knife-edge heater. These fixtures were held in place by tightly fitting rubber stoppers so that the vessel, when sealed, was steam tight. In addition, the lid was provided with six openings, each fitted with a one-holed rubber stopper of such size as to accommodate the standard Abel test-tube. The temperature of the water in the bath was raised to about 75° C. by means of a Bunsen burner and then increased to the required 76.7° C. by means of the knife-edge heater, and maintained at this value by means of the thermoregulator, which was of the usual type (filled with mercury and carbon tetrachloride).

Tests were carried out in duplicate using 0.5 gm. samples. These were first dried at 63° C. in an Abderhalden for one hour, then allowed to stand in an open dish at room temperature at a relative humidity of 55 to 65%. This ensured a moisture content of about 1%. The starch–iodide papers were standardized by testing a known sample of cellulose nitrate. The starch–iodide test paper was held in position in the Abel test-tube by means of a hooked glass rod inserted through a rubber stopper. After use, these glass hooks and rubber stoppers were boiled for a few minutes in a dilute solution of sodium hydroxide (0.5%) and then in distilled water. They were then dried at 50° C. on a piece of clean filter paper.

(b) The Bergmann–Junk Test

The nitrated starches were tested for stability by means of the Bergmann–Junk test using 0.5 gm. samples instead of the 2.0 gm. samples prescribed in the official test. Cellulose nitrate samples (0.5 gm.) were used as a standard. These Bergmann–Junk tests were carried out by the Department of Mines and Resources, Explosives Division, Ottawa, Canada.

Acknowledgments

The authors wish to thank the Canada Starch Co. for providing the starch used in these experiments and Mr. M. C. Fletcher, Chief Explosives Chemist, Department of Mines and Resources, Ottawa, under whose direction certain of the explosive tests reported herein were carried out by Dr. A. Gillies.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXI. PROPERTIES OF THE FRACTIONATED NITRATES OF TWO FRACTIONS OF CORN STARCH[1]

By W. R. Ashford, T. H. Evans, and Harold Hibbert

Abstract

Corn starch has been separated into two individual components, arbitrarily designated as amylose (linear fraction) and amylopectin (branched-chain fraction) by means of preferential adsorption on cellulose (Tanret–Pacsu method). These components have been nitrated and their nitrates fractionated by dissolution in ethanol. The relative stabilities and nitrogen contents of the nitrated fractions have been studied.

Unfractionated amylose nitrate has greater stability than unfractionated amylopectin nitrate as judged by the Bergmann–Junk test. Dissolution methods of fractionation showed a much higher solubility of the amylopectin nitrate, the greater relative stability of the amylose fractions, and the somewhat greater stabilizing action of ethanol in the case of the latter.

The widely different solubilities of amylose and amylopectin nitrates in conjunction with the lower ethanol solubility of whole starch nitrate are in accordance with the theory of a branched-chain structure for amylopectin and the linear type for amylose.

Introduction

Most of the earlier work (from 1833 on) on starch nitrate is concerned with methods of preparation, stabilization, and use in explosives, but no exhaustive investigation has been made with the object of providing a satisfactory explanation of its abnormal instability. Application of the customary procedures by which cellulose nitrates are stabilized proved of little or no value in the case of starch nitrates. The former are known to be essentially stable following removal of acidic and ester-type impurities.

The heterogeneity of all varieties of starch is apparent from the work of recent investigations (13, pp. 166-170) and it is to be expected that the nitrates of starch should be still more heterogeneous. The heterogeneity of cellulose is in one direction only, namely, in the matter of varying chain lengths, there being no tendency toward the formation of branched chains as with starch. With the former, the long chains are united laterally essentially by "hydrogen bonding" to give the crystalline micelle, whereas in starch only a small part of the total granule (the amylose) may have this type of structure.

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que. From a thesis presented to the Faculty of Graduate Studies and Research, McGill University, by W. R. Ashford in May 1943 in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] *Holder of a Fellowship under the National Research Council of Canada, 1942–43. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[3] *Sessional Lecturer, 1941–43, Division of Industrial and Cellulose Chemistry, McGill University. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[4] *Late Professor of Chemistry, Division of Industrial and Cellulose Chemistry, McGill University.*

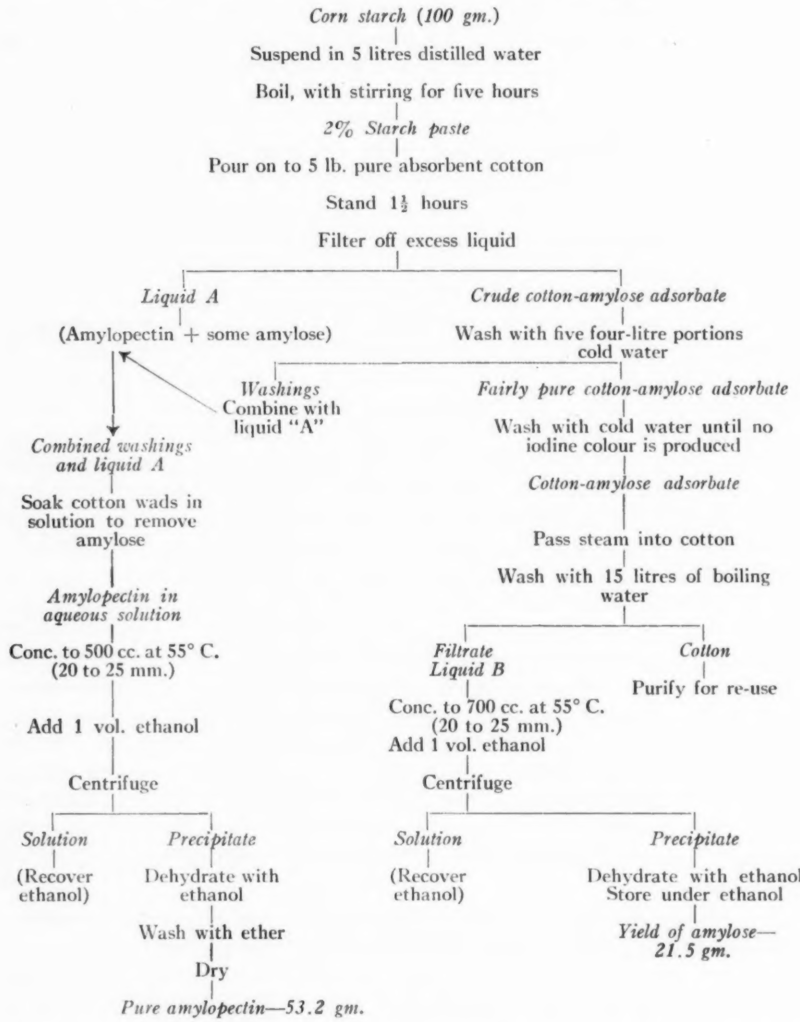
It was evident that no definite conclusions on starch nitrate stability was possible prior to a careful investigation of the properties of the nitrates prepared from the amylose and amylopectin portions of the starch granule (13, pp. 166-170), especially in view of recent improvements in methods of their isolation. This seemed all the more desirable in that, although much work has been done on the fractionation of cellulose nitrates (20), only little attention has been paid to the fractionation of starch nitrates. Berl and Kunze (3), using a freezing technique, separated starch nitrate into two components, which they claimed were amylose and amylopectin nitrates, respectively. Centola (5) separated amylose and amylopectin nitrates on the basis of their solubilities in ethanol, while the same principle was employed by Snelling (19) to obtain three fractions from whole starch nitrate.

Several methods have been used in an attempt to fractionate starch into its separate components and thus achieve some elucidation of its structure. These include precipitation of amylopectin from starch pastes by use of salts of the alkaline earths (24), treatment with superheated steam (15), treatment with water at 75° to 90° C. (8), centrifugation (7, 18), Ling and Nanji's freezing technique (2, 11), electrodecantation (6, 16, 22), ultrafiltration (22), and selective adsorption (14, 21). Two more recent methods of fractionation are those of Schoch (17, pp. 247–275) and a modification of same by Kerr (8; 9, pp. 129–178). The former is based on the selective precipitating action of *n*-butanol toward starch sols, two products of markedly different physical and chemical characteristics being obtained. The second method is similar except that the precipitant consists of a mixture of *n*-butanol and methanol. All methods employ swelling agents of various kinds which may bring about hydrolysis of the glucosidic linkages so that the products isolated may not be the true constituents of native starch. The selective adsorption method avoids the use of harsh swelling reagents and employs activated carbon, Fuller's earth, or cotton cellulose for the preferential adsorption of the amylose. The work herein described was carried out using the selective adsorption method (Fig. 1) with cotton cellulose as the adsorbent. The cotton-amylose adsorbate is formed instantaneously when a cold corn starch paste (2%) is brought into contact with cotton and can be washed free of amylopectin by cold water. The adsorbate is then readily decomposed by boiling water to give a clear solution of amylose. The dissolved amylose can be converted to the solid form by concentration of the solution followed by precipitation with alcohol.

The purpose of this fractionation of corn starch was to obtain, if possible, homogeneous products suitable for nitration, and the characteristics of the nitrates obtained indicate that this was accomplished to a considerable degree. In order to make possible a more thorough study of the properties of two of the components of starch (amylose, amylopectin) a fractionation of the nitrates of these two components was undertaken and a study made of the characteristics of the resulting products. To this end, fractional dissolution was employed. This method makes use of the different solubility character-

istics exhibited by fractions of different molecular weight and chemical constitution. Such fractions are usually present in high polymeric substances, especially those of natural occurrence, e.g., starch.

FIG. 1. FRACTIONATION OF STARCH BY THE ADSORPTION PROCESS



The solubility of a nitrated starch depends upon (i) its chain length, (ii) its degree of association and the power of the solvent to break associative bonds, and (iii) the nitrogen content. At the end of the nitration reaction

there is present a heterogeneous mass of varying chain lengths, degrees of association, and nitrogen contents. The use of fractional dissolution for the fractionation of starch nitrates permits a separation based on both physical and chemical properties. Shorter, non-associated chains, especially those of lower nitrogen content, are removed, leaving a product that may be visualized as a micellar mass formed of tightly interlocking chains. The dissolution method has the disadvantage that the process involves a heterogeneous system.

The following analytical methods were employed for the characterization of the nitration products.

(a) Nitrogen Content

Determinations of nitrogen content were made by two methods: (i) the Bowman–Scott method (4) using certain modifications; and (ii) the Dupont nitrometer method (10, pp. 401–423).

(b) Determination of Stability of the Nitrates

Many tests have been devised to measure the stability of the nitrated polysaccharides of the nitrocellulose type of explosive (12, pp. 644–660). In most of these the heat stability of the product under examination is measured. In the present investigation, the two most widely used tests, namely, the Abel heat test and the Bergmann–Junk test, have been employed. It is generally assumed that the Abel test indicates the physico-chemical condition of an explosive from the point of view of the ease of decomposition that may exist owing to the presence of minute amounts of foreign substances. The main objection to the Abel test is its extreme sensitiveness, the standard tint being produced by as little as 0.000135 mgm. of nitrogen peroxide. In the present work, the technique of the Abel test was simplified and all precautions taken (1). The heat test values obtained are therefore considered to represent the amount of impurity present in the sample at the time of the test and to indicate the initial stages of decomposition.

In contrast to the Abel test the Bergman–Junk test is quantitative and is not affected to nearly the same extent by added adulterants. Furthermore, it indicates the stability that may be expected over a long period of storage, since the products of decomposition are left in contact with the nitrate during the entire heating period. This test is also dependent upon the moisture content of the sample and is influenced by the presence of certain impurities such as urea.

The Bergmann-Junk test as applied to starch nitrates was modified in one respect only, namely, the size of sample used. Instead of the customary 2.0 gm. sample, amounts weighing 0.5 gm. were used and compared for stability with a similar quantity of cellulose nitrate.

The nitrates of amylose and amylopectin after subjection to fractional dissolution gave rise to products of varying nitrogen content, Abel heat value and Bergmann–Junk stability (Table I).

It is significant that 86.7% of the amylopectin nitrate was ethanol-soluble, whereas only 20% of the amylose nitrate was dissolved by the alcohol. A

TABLE I

FRACTIONAL DISSOLUTION OF AMYLOSE AND AMYLOPECTIN NITRATES AND CHARACTERISTICS OF THEIR PRODUCTS

Product	Weight, gm.	% of crude product	% N	Abel heat value	Bergmann–Junk*, mgm. of N_2
Amylose nitrate	60.0	100	12.96	10	7.28
Ethanol-insoluble amylose nitrate	46.0	79.5	13.28	40	2.62
Ethanol-soluble amylose nitrate	12.3	20.5	11.62	55	1.90
Amylopectin nitrate	60.0	100	12.25	4	15.20
Ethanol-insoluble amylopectin nitrate	6.9	13.3	12.58	16	3.74
Ethanol-soluble amylopectin nitrate	52	86.7	11.82	13	2.23

* *Mgm. of nitrogen evolved per 1.0 gm. sample of nitrate.*

high stability (Abel) was found with both the soluble and insoluble amylose nitrate fractions, those of the corresponding amylopectin nitrates being less stable. Prior to testing, all traces of ethanol were carefully removed by repeated boiling in distilled water, drying, and extraction with petroleum ether. The Bergmann–Junk tests confirmed these Abel heat test results in that the amylose nitrates had a higher stability than the amylopectin nitrates. It is of interest that the treatment of crude amylopectin and amylose nitrates with ethanol in the fractionation process actually brought about an increase in the stability of both the alcohol-soluble and alcohol-insoluble fractions.

In a previous paper dealing with whole starch (1) it was found that only about 10 to 20% of the whole starch nitrate could be extracted by use of ethanol as a solvent, whereas, as pointed out above, amylopectin nitrate treated independently with ethanol is 86% soluble and the amylose nitrate about 20% soluble. One explanation for this is that in the case of the whole starch nitrate, the solvent is unable to break associative bonds necessary for solution, while, when the amylopectin is separated from the amylose, associative bonding is greatly lessened and solution of the former component can take place more readily.

Amylose nitrate is no more soluble than whole starch nitrate because it is responsible for the associative bonding in whole starch. This conclusion is based upon a highly branched structure for amylopectin and a linear, non-branched structure for amylose or, conversely, the solubility results herein reported can be taken as evidence for the branched and non-branched structures for amylopectin and amylose, respectively.

In the paper referred to above (1), the problem was to obtain, if possible, a stable starch nitrate, either by removal of unstable fractions by ethanol solution or by the stabilizing action of ethanol. That it would be extremely difficult or impossible to remove the less stable portions of starch nitrate by ethanol dissolution is evident from the results herein reported, when it is

observed, first, that those less stable portions consist of amylopectin nitrate which, by present theories, constitutes about 75% of the starch molecule, and second, that only 10 to 20% of whole starch nitrate was found to be ethanol-soluble.

The fact that fractional dissolution in ethanol did bring about increased stability in starch nitrate would seem to indicate that the 10 to 20% of material removal by ethanol dissolution was mainly amylopectin nitrate.

Experimental

Fractionation of Corn Starch

Corn starch (100 gm.) was added to five litres of distilled water and the mixture boiled for five hours to ensure complete rupture of the granules (Fig. 1). Five pounds of pure absorbent cotton was introduced into the starch solution and allowed to stand for one and one-half hours at room temperature. The paste-soaked cotton was then placed in a large earthenware filter and the liquid remaining from the five litres of starch solution removed by suction filtration. The filtrate (Liquid *A*) was reserved for future work. The cotton was washed with five four-litre portions of cold distilled water, and the wash waters added to the original filtrate. The cotton was washed with further portions of cold, distilled water until the filtrate gave no colour with iodine, indicating absence of amylopectin. The cotton was then subjected to live steam, while still on the filter, and suction applied. The hot, moist cotton was treated repeatedly with boiling water, using a total of about 15 litres, in order to remove the adsorbed amylose. The filtrate (Liquid *B*) gave a bright blue colour with iodine. The absorbent cotton can be used repeatedly.

Liquid *B*, containing the amylose fraction, was concentrated to about 700 to 800 cc. at a bath temperature not exceeding 55° C., and the amylose precipitated quantitatively by the addition of an equal volume of ethanol. The product was separated by centrifuging as a fine, white precipitate and was readily dehydrated by the use of 80% ethanol followed by a further centrifuging and by grinding under absolute ethanol. The final product, a white powder, was stored in ethanol to prevent drying and consequent retrogradation. Yield of dry product (calculated by drying an aliquot portion) was 21.5 gm.

Liquid *A*, the amylopectin fraction, was freed from amylose by adsorbing the latter on pieces of cotton. When a hot water extract of a piece of cotton, which had been washed with cold water, no longer gave a blue iodine colour reaction, the complete removal of amylose was indicated. The 20 litres of solution were then concentrated at 50 to 55° C. (20 to 25 mm.) to 500 cc. The addition of an equal volume of ethanol caused precipitation of a flocculent, sticky mass of amylopectin. The product was centrifuged and dehydrated with ethanol, washed with ether, and dried in a desiccator. Yield, 53.2 gm.

Nitration of Amylose and Amylopectin

(*a*) *Preparation of nitric acid.*—Colourless nitric acid (98.6%) was prepared as required by distillation (60 to 70° C., 20 to 30 mm.) from a 1:1 mixture of nitric (1.42 sp. gr. or commercial fuming nitric) and concentrated sulphuric acids (1.84 sp. gr.) in an all ground-glass set up.

(*b*) *Nitration procedure.*—Nitrations were carried out according to the Will and Lenze method (23) as described previously (1). Yields amounted to 160 to 170% for amylose and amylopectin (% yields are based upon the theoretical value for starch nitrate (182.7 gm. from 100 gm. starch)).

Fractional Dissolution of Amylose and Amylopectin Nitrates

Sixty grams of each nitrate was placed in a litre of ethanol (98 to 99%) and stirred for a period of 10 hr. at room temperature, and the residue separated by centrifuging and filtration. The ethanolic extract in each case was evaporated to small volume (30 to 35° C., 20 to 25 mm.). In the case of the amylopectin extract, the nitrate was precipitated by the addition of petroleum ether (30 to 50° C.) and in the case of the amylose extract by the addition of water. The extracted nitrates were placed in two litres of distilled water and the solution boiled under a reflux condenser for 12 hr. in order to replace the solvent. In similar manner, the residues left undissolved by ethanol were treated by boiling in water for 12 hr. to remove ethanol. Weights and proportions of the two fractions are shown in Table I.

Nitrogen Content and Stabilities

These two characteristics of the nitrated products were determined as outlined in a previous paper (1). Their values are given in Table I.

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LIQUID–VAPOUR EQUILIBRIUM FOR THE SYSTEM ETHANOL–ACETONE[1]

By A. R. Gordon[2] and W. G. Hines[3]

Abstract

Vapour pressures and equilibrium liquid–vapour mole fractions have been determined for the solvent system ethanol–acetone at 32°, 40°, and 48° C. in a modified form of the apparatus developed by Ferguson and Funnell. It is shown that the data are consistent with the Gibbs–Duhem equation if it be assumed that deviations from ideality in the vapours may be computed from the principle of Corresponding States. It is also shown that the variation of the activities of the components in the liquid with temperature is in moderate agreement with the heat of mixing data for the system.

The work reported here was undertaken to provide liquid–vapour equilibrium data for the important solvent system ethanol–acetone. The majority of such studies reported in the literature have involved some sort of distillation procedure. The possible sources of error in such measurements are now well understood—superheating of the liquid, lack of equilibrium between liquid and vapour, reflux in the apparatus, entrainment of droplets of liquid in the vapour given off, etc.; the elaborate modification of the familiar Sameshima apparatus used by Scatchard and Raymond (11) in their study of the system ethanol–chloroform is an example of the precautions to be taken if accurate results are to be obtained. In 1929, Ferguson and Funnell (2) reported a novel and much improved form of the apparatus developed by Rosanoff *et al.* (8, 9); in a closed all-glass system, the vapour was continuously circulated through the liquid until equilibrium was attained, the vapour and liquid phases were separated, the vapour condensed, and both phases analysed; the apparatus used here is a modification of theirs, and (we believe) an improvement on it.

There is an additional complication with the system ethanol–acetone since analysis by refractive index or density is not practical, while chemical methods are excluded if reasonable accuracy is desired. The compositions of the liquid and condensed vapour were therefore determined by measuring their vapour pressures, previous independent measurements having fixed the vapour pressure curve for the system. Under the most unfavourable conditions (low temperature and high acetone concentration) a precision of 0.1 mm. of mercury corresponds to 0.08 mole % in the composition, and under the most favourable to about one-sixth of this.

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Contribution from the Chemistry Department, University of Toronto, Toronto, Ont.
[2] *Professor of Chemistry.*
[3] *Research Assistant. Present address: Research Enterprises, Toronto, Ont.*

Experimental

The apparatus is shown in Fig. 1. Essentially, it consists of a bulb A, of approximately 75 cc. capacity, containing the liquid phase, and immersed in a covered water thermostat regulated to 0.002° C.; the vapour is circulated through the liquid in A by the all-glass, electrically operated Funnell–Hoover

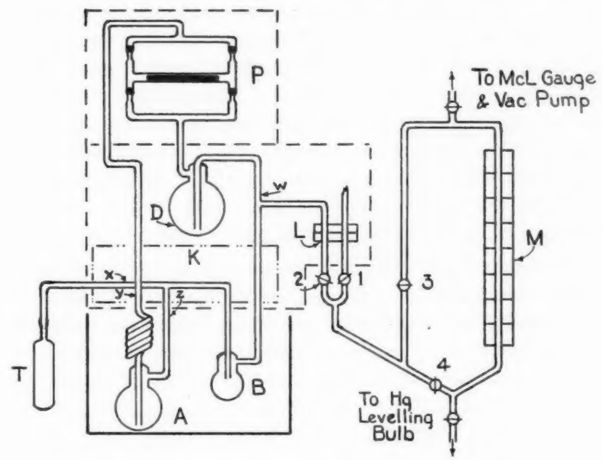

FIG. 1.

(3) pump P, thence through the small bulb B and finally through the large bulb D (of 13 litres capacity). The vapour part of the apparatus is enclosed in a double-walled air-bath whose temperature is held 0.5° C. higher than that of the water-bath; the pump P (capacity 12 litres per hr.) is in a separate compartment maintained at a temperature 2° C. higher than that of the main air-bath. The glass tubes running from A above water level to the air-bath are thermally shielded by heavy double-walled copper tubes, the space between the tubes being packed with rock wool. K indicates a copper box with separate double-walled door, to permit momentary access to this part of the apparatus without disturbing the temperature of the main air-bath. All glass tubing in the apparatus was of 8 mm. internal diameter to ensure rapid circulation of the vapour. The levelling line L of the manometer was viewed through a double glass window, while the manometer scale M was of silvered plate glass, ruled by the dividing engine in the Physics Department of this University, and checked by microscope comparator. Not shown in Fig. 1 is a small glass jar enclosing the bulb B and connected to the main water-bath by a siphon; a very small electric heater in the jar maintains the temperature of B during a run slightly above that of A. Bath temperatures were read on Beckmann thermometers set against laboratory standards that had been calibrated by means of a platinum resistance thermometer with National Bureau of Standards certificate.

In carrying out a measurement, usually from 20 to 30 gm. of an ethanol–acetone solution was placed in the filling tube T, which was fitted with a standard taper joint; the sample was then frozen with liquid air. With the mercury in the manometer just above tap 4, and with taps 2 and 3 open, the apparatus was evacuated; tap 3 was then closed, the sample melted and frozen again, and any air resulting pumped off. This was repeated, usually three or four times, until the residual pressure after melting and freezing was not greater than 0.001 mm. as measured on the McLeod gauge. The sample was then distilled into A, frozen with liquid air, and T was sealed off with a burner at x. The air-bath was brought on temperature, the mercury raised to the level L, tap 3 was closed, and the vacuum reading on the manometer scale M was taken. The air-free sample was thus enclosed in an all-glass apparatus in which the vapour was not in contact with any stopcock and in which the only mercury–glass contact, that at L, could be maintained, with proper manipulation, practically stationary throughout the experiment.

The water-bath was then filled and brought on temperature, and the pump started. When constancy of pressure had shown that equilibrium had been attained (this usually required from four to six hours) the pump was stopped and the equilibrium vapour pressure was read; after circulating the vapour for another 30 min., a second reading was taken with P stopped, and after a further 30 min., a third; to be accepted the three successive readings had to agree within 0.1 mm. The pump was then stopped, and the bulb A was sealed off from the rest of the apparatus at y and z, thus separating the liquid and vapour. After draining the water-bath, the vapour was condensed into B with liquid air, and B was then sealed off from D at w; after the trace of non-condensable gas had been pumped off, the water-bath was filled and brought on temperature, and the vapour pressure of the condensed vapour was taken.

To interpret such pressure readings in terms of composition, the vapour pressure curve for the system must be known. A weighed sample of gravimetrically known composition (from 20 to 30 gm.) after being outgassed was distilled into a flask similar to A with liquid air, the flask then being sealed off from its filling tube; this flask connected directly to the manometer through tap 1. When the water-bath had been filled, the vapour pressure was read after temperature equilibrium had been attained. There is one correction that must be made, however, before such readings may be used to fix the vapour pressure curve. Part of the weighed sample evaporates, and, although the amount is small in comparison with the liquid, its composition is different from that of the liquid whose vapour pressure has been determined, i.e., the composition of the actual liquid will be slightly different from that of the sample distilled into the apparatus. As a first approximation, this was neglected, and a provisional vapour-pressure–liquid-composition curve was drawn; from this and the vapour–liquid equilibrium measurements, a provisional curve of vapour composition as a function of liquid composition was obtained. Since the volume involved in the vapour pressure measurements was known, viz., 212 cc. less the volume of the sample weighed out, it was now

possible to make an approximate calculation of the weight and composition of the vapour above the liquid in the vapour pressure measurements and so arrive at the true composition of the liquid whose vapour pressure had been determined. In extreme cases, the true liquid composition differed by as much as 0.3 mole % from that of the sample that had been introduced into the apparatus. From this corrected vapour pressure curve, a corrected liquid-vapour composition curve was obtained, allowance now being made for the vapour above the condensed vapour when the vapour pressure of the latter was read. Calculation showed that a third approximation was not necessary.

The alcohol was 99.5% absolute, refluxed under nitrogen with magnesium and a trace of iodine for 15 hr., and distilled, the first and last fractions being rejected. The acetone was Shawinigan A.R. grade; after refluxing under nitrogen with potassium permanganate for six hours, it was distilled, the middle 60% being retained and redistilled. The final distillate was allowed to stand over anhydrous sodium carbonate for 24 hr., then siphoned through glass wool into a storage flask containing Drierite that had been activated at 140° C. under vacuum for 24 hr.; samples were distilled under vacuum from the storage flask into the weighing tubes. The manometer mercury was acid washed and twice distilled under vacuum.

Results

The vapour pressure measurements are recorded in Table I, and the liquid-vapour equilibrium results in Table II; in the tables P stands for the pressure in millimetres of mercury reduced to 0° C. and N_1 and N_1' for the liquid and vapour mole fractions of acetone respectively. From large-scale deviation plots of these data, values of P and of N_1' were obtained for round values of

TABLE I

VAPOUR PRESSURE MEASUREMENTS

32° C.		40° C.		48° C.	
N_1	P	N_1	P	N_1	P
0	87.6	0	134.2	0	200.8
0.0422	112.5	0.0389	162.1	0.0507	244.7
0.0673	124.4	0.0446	165.1	0.1234	297.2
0.1130	145.2	0.0765	184.0	0.1634	321.8
0.1787	169.3	0.1409	219.1	0.3179	394.5
0.2361	186.1	0.1883	240.1	0.4410	438.9
0.2665	191.9	0.2683	270.3	0.5601	474.3
0.3128	205.4	0.3406	292.8	0.7063	511.6
0.3470	212.8	0.4355	318.5	0.8218	537.9
0.4458	232.8	0.5315	340.6	1.0000	572.3
0.5372	247.8	0.6528	366.0		
0.6548	265.3	0.7727	388.0		
0.7721	281.9	0.8593	402.9		
0.8474	291.7	0.9038	410.2		
0.9252	301.0	1.0000	424.9		
1.0000	309.9				

N_1 and are given in Table III; with very few exceptions, the experimental points from Tables I and II differed from the smooth curves corresponding to Table III by less than 0.2 mm. in the pressure and by less than 0.002 in N_1'.

TABLE II

EQUILIBRIUM LIQUID–VAPOUR COMPOSITIONS

32° C.		40° C.		48° C.	
N_1	N_1'	N_1	N_1'	N_1	N_1'
0.0255	0.1630	0.0265	0.1515	0.0205	0.1005
0.0410	0.2350	0.0285	0.1565	0.0395	0.1770
0.0700	0.3360	0.0520	0.2525	0.0440	0.1960
0.1020	0.4195	0.0875	0.3420	0.0735	0.2850
0.1565	0.5120	0.0955	0.3685	0.1185	0.3830
0.2250	0.5970	0.1395	0.4540	0.1965	0.5035
0.2580	0.6260	0.2215	0.5590	0.2015	0.5090
0.3335	0.6835	0.2640	0.6030	0.2550	0.5615
0.3865	0.7160	0.3260	0.6470	0.3670	0.6500
0.4795	0.7605	0.3710	0.6750	0.5080	0.7375
0.6245	0.8280	0.4745	0.7360	0.6430	0.8085
0.6895	0.8565	0.6200	0.8035	0.7285	0.8525
0.8430	0.9240	0.7565	0.8680		
0.8720	0.9380	0.8735	0.9290		

TABLE III

N_1	32° C.		40° C.		48° C.	
	N_1'	P	N_1'	P	N_1'	P
0	0	87.6	0	134.2	0	200.8
0.025	0.1605	102.7	0.1435	152.2	0.1210	223.3
0.050	0.2700	116.2	0.2460	168.5	0.2155	244.1
0.075	0.3505	128.3	0.3205	183.3	0.2890	263.6
0.10	0.4130	139.7	0.3795	197.4	0.3460	281.6
0.15	0.502	159.5	0.470	223.3	0.437	314.2
0.20	0.569	175.9	0.538	244.9	0.507	341.5
0.25	0.619	190.1	0.590	263.9	0.560	365.5
0.30	0.660	202.4	0.631	280.6	0.602	387.0
0.40	0.722	223.8	0.694	309.0	0.670	424.9
0.50	0.773	242.0	0.747	334.0	0.731	457.4
0.60	0.817	257.4	0.795	355.5	0.785	485.0
0.70	0.859	271.9	0.843	375.1	0.838	510.1
0.80	0.902	285.3	0.893	393.0	0.889	533.0
0.90	0.950	297.9	0.945	409.4	0.942	553.6
1.00	1.000	309.9	1.000	424.9	1.000	572.3

Our vapour pressures for ethanol, viz., 87.6, 134.2, and 200.8 mm. at 32°, 40°, and 48° C. are definitely below those recorded in International Critical Tables (4, p. 217), which correspond for these three temperatures to 88.0, 135.3, and 201.7 mm. respectively. They may be compared with those given by Scatchard and Raymond's corrected equation (12) for the same

three temperatures, 87.4, 134.1, and 200.7 mm. The vapour pressures recorded for acetone in the literature are not at all concordant, as has been pointed out by Beare, McVicar, and Ferguson (1); our results for the two lower temperatures agree most closely with those of Price (7) and for 48° C. with that of Sameshima (10).

One check on the self-consistency of the experimental data may be obtained from the familiar Gibbs–Duhem equation. If the customary assumption (justified for the small range of pressures involved) be made that the thermodynamic potentials μ_1 and μ_2 of the acetone and the ethanol in the liquid phase are independent of pressure, then for constant temperature

$$N_1 \, . \, d\mu_1 + N_2 \, . \, d\mu_2 = 0. \tag{1}$$

If the equilibrium vapour be assumed to obey the equation of state

$$P(V - n_1'\beta_1 - n_2'\beta_2) = (n_1' + n_2')RT, \tag{2}$$

where n_1' and n_2' are the moles of acetone and ethanol in the vapour and β_1 and β_2 the corresponding second virial coefficients, it is easy to show (11) that Equation (1) may be written

$$d \ln P = \frac{(N_1' - N_1)}{N_1'(1 - N_1')} \, . \, dN_1' - \frac{(N_1\beta_1 + N_2\beta_2) \, . \, dP}{RT} \, . \tag{3}$$

Thus if the vapour pressure of one pure component and the virial coefficients be known, it is possible by integration and successive approximation to compute the entire vapour pressure curve for the system from a knowledge of the equilibrium liquid and vapour mole fractions.

For neither acetone nor ethanol are vapour density data available of accuracy sufficient to fix the β's; in a similar situation, Scatchard and Raymond (11) appealed to the principle of Corresponding States and in particular to the equation of Keys, Smith, and Gerry (6):

$$\beta(P_c/T_c) = 11.5 - (24.78/T_r) \times 10^{0.1930/T_r^2} \, , \tag{4}$$

where P_c and T_c are the critical pressure and temperature and T_r is the reduced temperature. For acetone, the critical temperature and pressure are 508° K and 47 atm., respectively, while for ethanol the corresponding values are 516° K and 63 atm. (4, p. 248); the resulting values of β_1 and β_2 in cubic centimetres per mole from Equation (4) are

	32° C.	40° C.	48° C.
Acetone	−1405	−1275	−1165
Ethanol	−1130	−1025	− 935

If these values are used in Equation (3), the agreement is not satisfactory; Scatchard and Raymond (11) found the same to be true for the system ethanol–chloroform, and accordingly multiplied both coefficients by the same arbitrary factor for a given temperature, viz., 2.2, 1.65, and 1.5 for 35°, 45°, and 55° C., respectively. This is obviously equivalent to assuming that Equation (4) gives the correct ratio for the coefficients but not their absolute

values, and has the advantage that in checking the experimental results by means of Equation (3) there is only one adjustable parameter—the factor r by which the corresponding states β's have been multiplied. Fig. 2 shows the result of the same procedure here; the continuous curves in the figure correspond to the integration of Equation (3) when the values of r selected are 2.7, 1.8, and 1.2 for 32°, 40°, and 48° C., respectively; P_2° is the vapour pressure

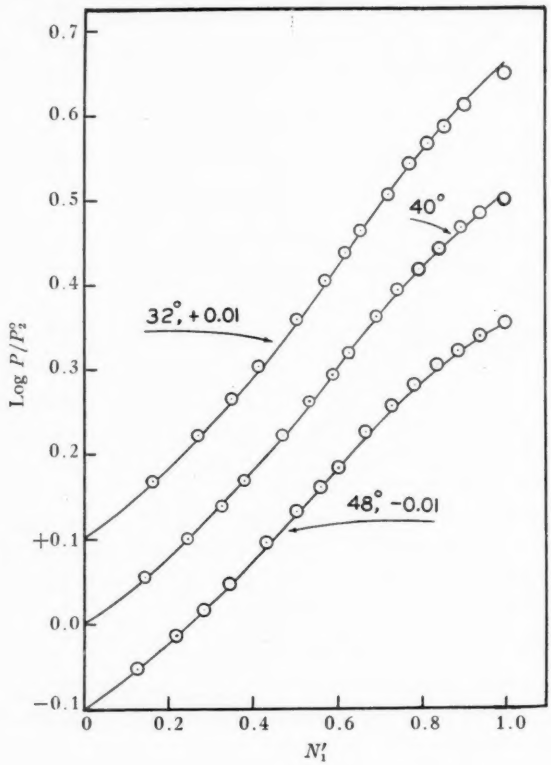

FIG. 2.

of pure ethanol for the given temperature, corresponding to the lower limit of integration, and the circles indicate the vapour pressures recorded in Table III. The values of r used are of the same order of magnitude as those of Scatchard and Raymond although they decrease more rapidly with rising temperature than do theirs. As the figure shows, the agreement is moderate, in general within 0.005 in the common logarithm, and is probably as close as can be expected in view of the uncertainty as to the equation of state on the one hand, and the precision of the data on the other.

There is another check that may be applied to the data. The activity a_1 of the acetone in a solution is given by

$$\ln a_1 = \ln N_1'P/P_1^\circ + r\beta_1(P - P_1^\circ)/RT, \tag{5}$$

where P_1° is the vapour pressure of pure acetone and r is the arbitrary factor by which the corresponding states virial coefficients have geen multiplied; see above. Since

$$\partial \ln a_1/\partial T = (H_1^\circ - H_1)/RT^2, \tag{6}$$

where H_1° is the molal heat content of pure acetone and H_1 is the partial molal heat content of acetone in the solution, it is possible by integration of Equation (6) to calculate the activity at one temperature from the activity in the same solution at another temperature provided $(H_1^\circ - H_1)$ is known for the temperature range. From the heat of mixing data for this system (5, p. 156), it is possible to obtain for 25° C. the values of $(H_1^\circ - H_1)$ and $(H_2^\circ - H_2)$ entered in Table IV. If it be assumed that these are valid for the

TABLE IV

N_1	0.1	0.2	0.4	0.6	0.8	0.9
$(H_1^\circ - H_1)$, cal.	−900	−680	−380	−210	− 60	− 10
$(H_2^\circ - H_2)$, cal.	− 10	− 50	−170	−350	−700	−960
N_1' calc., 32° C.	0.412	0.569	0.717	0.811	0.900	0.948
P calc., 32° C.	137	173	221	256	285	298
N_1' calc., 48° C.	0.349	0.507	0.671	0.780	0.886	0.942
P calc., 48° C.	281	342	425	485	533	554

range 32° to 48° C. (this is obviously equivalent to assuming that the molar heat capacity for ethanol–acetone solutions is linear in the mole fraction) one can obtain at once values of a_1 at 32° C. and at 48° C. from that at 40° C. From this and a similar calculation for a_2, it is then possible, since P_1°, P_2°, and r are known, to solve for N_1' and P by a short series of approximations. The results of such calculations are given in Table IV in the lines labelled N_1' calc. and P calc. A comparison of Table IV with Table III shows that the agreement for N_1' is reasonably satisfactory; in only one instance is the discrepancy greater than 0.5 mole %. The agreement with respect to the pressures is also as close as can be expected except possibly for the solutions low in acetone at 32° C.

It would seem safe to say that our results are not inconsistent with the Gibbs–Duhem equation on the one hand and the thermal data on the other. We therefore feel that while the precision of the data may not be as great as one could wish, Table III cannot be very seriously in error.

Acknowledgment

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LIQUID-VAPOUR EQUILIBRIUM FOR THE SYSTEM ETHANOL-DIETHYL-ETHER[1]

A. R. GORDON[2] AND W. J. HORNIBROOK[3]

Abstract

Vapour pressures and equilibrium liquid–vapour mole fractions for the system ethanol–ethyl-ether have been determined at 25° C. in the apparatus previously employed for the system ethanol–acetone. The measured vapour pressures deviate from those reported in the literature by more than the apparent precision of the measurements. The type of equation of state for the vapour that must be assumed in order to make the data consistent with the Gibbs–Duhem equation is discussed.

In this paper we report vapour pressures and equilibrium liquid–vapour mole fractions for the system ethanol–diethyl-ether at 25° C. Louder, Briggs, and Browne (4) have determined the vapour pressure curve for this system over a range of temperatures, but there is no information in the literature as to the composition of the vapour in equilibrium with a given liquid. This system provides an interesting contrast to that studied in the preceding paper owing to the relatively great difference in the vapour pressures of ethanol and ether.

Experimental

The apparatus, the experimental technique, the method of analysis, the corrections to be applied, and the method of purifying the ethanol have been described in detail (1). The ether was Analar grade; it was first shaken with 50% by weight sulphuric acid, decanted, and shaken with calcium oxide in order to dry it and free it from suspended acid. It was then refluxed with sodium wire in an atmosphere of carefully dried nitrogen until the addition of 1 gm. of benzophenone through the reflux condenser turned the entire liquid blue. The reflux condenser was drained, and the ether was then distilled into its container through a down condenser, care being taken that the atmosphere in contact with the ether at all times was dry nitrogen. It was stored in a two litre balloon flask under a slight positive pressure of dry nitrogen.

Results

The vapour pressure measurements are summarized in Table I and the liquid–vapour composition measurements in Table II. It should be noted that the analysis of the liquid phase and the condensed vapour by means of their vapour pressures is much more sensitive here than in the case of the system ethanol–acetone, particularly for solutions high in ethanol. In the tables, P is the pressure in millimetres of mercury reduced to 0° C., and N

[1] *Manuscript received March 23, 1946.*
Contribution from the Chemistry Department, University of Toronto, Toronto, Ont.
[2] *Professor of Chemistry.*
[3] *Research Assistant. Present address: Canadian Industries Limited, Montreal.*

TABLE I

VAPOUR PRESSURE MEASUREMENTS

N	0	0.0506	0.1018	0.1547	0.2370	0.2874	0.3745
P	58.9	125.7	183.2	232.6	294.3	323.9	365.9
N	0.4338	0.5175	0.6308	0.7958	0.9052	1.0000	—
P	388.6	416.1	446.6	484.1	510.1	535.8	—

TABLE II

EQUILIBRIUM LIQUID–VAPOUR COMPOSITIONS

N	0.0128	0.0322	0.0577	0.1104	0.2239
Y	0.2392	0.4420	0.5860	0.7235	0.8395
N	0.3260	0.5255	0.7710	0.9700	—
Y	0.8775	0.9155	0.9510	0.9918	—

and Y are the mole fractions of the ether in liquid and vapour, respectively. From large-scale deviation plots of the data, the values of Y and P for round values of N, entered in Table III, were obtained. It might be noted in passing

TABLE III

N	Y	P	N	Y	P
0	0	58.9	0.25	0.852	302.2
0.005	0.1105	66.0	0.30	0.870	330.7
0.01	0.1985	73.1	0.35	0.883	355.4
0.02	0.3305	86.7	0.40	0.893	376.1
0.04	0.4950	112.8	0.50	0.911	410.6
0.06	0.5940	137.3	0.60	0.925	438.9
0.08	0.6600	160.1	0.70	0.939	462.5
0.10	0.7070	181.3	0.80	0.956	485.2
0.15	0.7815	228.5	0.90	0.976	509.2
0.20	0.8245	268.8	0.95	0.988	522.2
—	—	—	1.00	1.000	535.8

that a convenient deviation function, suitable for correlating and interpolating the composition data, is defined by

$$Y = 0.9860N/(N + 0.0395) + \delta\,, \tag{1}$$

the resulting δ being less than 0.003 for values of N up to 0.35; for the higher ranges of concentration, deviations obtained by subtracting from Y a suitable linear function of N are adequate.

Our measured vapour pressure for pure ethanol at this temperature is somewhat below that given in International Critical Tables (59.0 mm.) and is definitely below that reported by Louder, Briggs, and Browne, viz., 59.7 mm.; it is 0.2 mm. above that given by Scatchard and Raymond's corrected vapour pressure equation (5). Our result for pure ether, 535.8 mm., lies

below the International Critical Tables (2, p. 288) value and that of Louder, Briggs, and Browne (537 mm.). A comparison of our values of the vapour pressures for the solutions with those of Louder, Briggs, and Browne shows that for solutions up to 60% by weight (48 mole %) their results lie from 1 to 3 mm. below ours; for their three solutions strongest in ether, however, their values are from 2 to 4 mm. above ours. This eliminates a difference in temperature in the two researches as a cause of the discrepancy, and suggests (as do the vapour pressures of the pure components) that the raw materials used in the two laboratories were different.

A check on the data by means of the Gibbs-Duhem equation

$$N \,.\, d\,\mu_1 + (1 - N) \,.\, d\,\mu_2 = 0\,, \tag{2}$$

where μ_1 and μ_2 are the potentials of the ether and the ethanol in the liquid, requires a knowledge of the equation of state of the vapour. In the absence of vapour density data for the gaseous solutions, the second virial coefficients β_1 and β_2 may be computed, as was done in the case of the system ethanol–acetone, by means of the principle of Corresponding States from the equation of Keyes, Smith, and Gerry (3); see Equation (4) of the preceding paper. The critical temperatures for ether and ethanol are 467° and 516° K, respectively, and the corresponding critical pressures 35.5 and 63 atm. (2, p. 248); the resulting values of β_1 and β_2 are -1367 and -1236 cc. per mole. Integration of the Gibbs–Duhem equation with these values of the coefficients (see Equation (3) of the preceding paper) shows however that the vapour pressure curve calculated from the Y–N data lies *above* the observed vapour pressures. This is in contrast to the system ethanol–acetone where the calculated curve was too low, and a reasonable fit could be achieved by multiplying both the corresponding states β's by a common factor greater than unity. This suggests that the more general equation of state (5)

$$V/(n_1 + n_2) = RT/P + Y\beta_1 + (1 - Y)\beta_2 + Y\,(1 - Y)\epsilon \tag{3}$$

be employed, where n_1 and n_2 are the moles of ether and ethanol in the vapour, $\epsilon = 2\,\beta_{12} - \beta_1 - \beta_2$, and β_{12} is the cross-virial coefficient. The potential of the ether in the vapour, μ_1', is then given by

$$\mu_1' = \mu_1^{\circ\prime} + RT \ln PY + \beta_1 P + \epsilon(1 - Y)^2 P, \tag{4}$$

where $\mu_1^{\circ\prime}$ is a function only of the temperature, with an analogous expression for the potential of the ethanol. If it be assumed that the potentials in the liquid are independent of pressure, substitution of the expressions (4) in Equation (2) gives

$$d \ln P = \frac{Y - N}{Y\,(1 - Y)} \,.\, dY - \frac{[\beta_1 N + \beta_2\,(1 - N)] \,.\, dP}{RT}$$
$$- \frac{\epsilon}{RT} \,.\, [N(1 - Y)^2 + (1 - N)Y^2 + 2Y(1 - Y)]\, dP\,. \tag{5}$$

Equation (5) is a simplified form of Scatchard and Raymond's (5) Equation (6) since in obtaining the last term of Equation (5), $2\,(Y-N)\;P\,.\,dY/dP$ has been replaced by its approximate value $2Y\,(1-Y)$, i.e., third order terms have been neglected.

The result of integrating Equation (5) with $\beta_1 = -1367$ cc., $\beta_2 = -1236$ cc., and $\epsilon = 4280$ cc. is shown by the continuous curve of Fig. 1; the circles correspond to the entries in Table III, and P_2° is the vapour pressure of ethanol. The value selected for ϵ corresponds to $\beta_{12} = 840$ cc., a not unreasonable value, and the figure shows that except for the highest points, the agreement between calculated and observed vapour pressure is moderately satisfactory. Not too much stress must be placed on this, however. One would expect, by analogy with the results for ethanol–acetone, that the values of the second virial coefficients computed by Keyes, Smith, and Gerry's

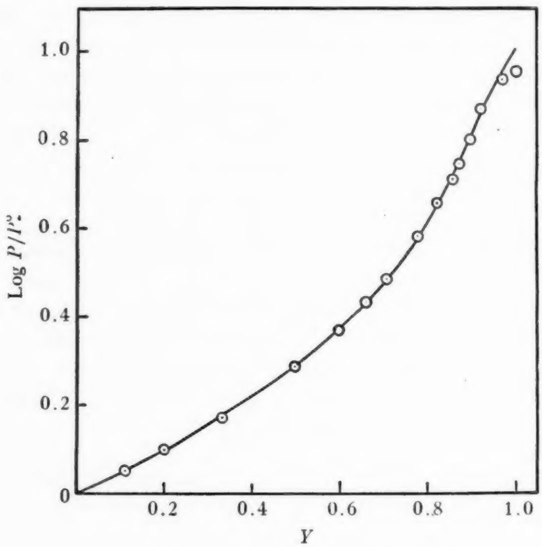

FIG. 1.

equation would be too low. If β_1 and β_2 are both arbitrarily multiplied by 3 (cf. the values of r used in the preceding paper) and ϵ be set equal to 8600 cc., i.e., $\beta_{12} \backsim 400$ cc., the resulting calculated curve is practically indistinguishable on the scale of the figure from the curve as printed. In other words, the use of two adjustable parameters—the arbitrary factor by which corresponding states β's are multiplied, and the value selected for β_{12}—reduces the attempt to check the data by means of the Gibbs–Duhem equation to little more than an exercise in curve fitting. Nevertheless, we believe that the results indicate that an equation of state of the type (3) is more suitable for this system than the simpler form used for ethanol–acetone.

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